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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

ZHENGHE HAN et al.

Serial No.: 10/541,296

Filed: July 6, 2005

For: SURFACE MODIFICATION
METHOD IN FABRICATING HIGH
TEMPERATURE SUPER
CONDUCTIVE DEVICES

Art Unit: 1793

Examiner: Paul A. Wartalowicz

APPELLANT'S RESPONSE

Honorable Commissioner of Patents & Trademarks
P.O. Box 1450
Alexandria VA 22313-1450

Dear Sir:

In response to the Examiner's Answer dated April 5, 2010, submitted herewith are copies of selected portions of "Thin Film Processes", edited by John L. Vossen and Werner Kern and published by the Academic Press, Inc. in New York (R1) and "Ion Bombardment Modification of Surfaces: Fundamentals and Applications", edited by Orlando Auciello and Roger Kelly, published by Elsevier in Amsterdam in 1984 (R2). These two reference documents R1 and R2 will be utilized in Applicant's arguments which are set forth herein below.

Without going into the detail of each and every rejection presented by the Examiner, Appellant respectfully submits that essentially it is the Examiner's opinion, which is not supported by any documentation, that a particle beam generated by a plasma sputtering device is substantially the same as an ion beam, that the properties in the product produced by the utilization of an ion beam would be substantially or inherently the same as that of a plasma sputtering device and the product produced utilizing the plasma sputtering device has no advantages over one produces with an ion beam. Accordingly, it is the Examiner's opinion that Applicant's claims are all anticipated or obvious over the art cited by the Examiner.

In reply to this position by the Examiner, Appellant respectfully submits that a plasma sputtering beam and an ion beam are not equivalent. In particular, each have different properties and Appellant respectfully submits that plasma sputtering has advantages over ion beams. These two issues will be discussed at length below.

In particular, Appellant respectfully submits that for the ion beam generated from ion guns (also called ion sources), a low background gas pressure is usually maintained of about 0.1 Pa or lower to minimize divergence of the beam and contamination (see R1, page 187, lines 35 and 36). Since the ion beam operates in a low background gas pressure, the energetic ions will travel a sufficient distance along a free path without collisions with the gas molecules. Therefore, the ion flux and the ion energy are independently controlled and the direction of ion impact on the surfaces is controlled (see R2, page 130, lines 19-23). Also, Appellant respectfully submits that a focus system of the ion source can decrease the divergence of the ion beam. For example, in a normal condition, the plasma edge beside the grid system in ion guns could form a proper shape, which gives the ion beam an initial convergence. Acceleration of the ions takes place mainly in the extraction region in the ion guns, since this is usually where the greatest potential drop occurs (see R1, page 183, lines 24-25). As a result, any ions leaving the discharged plasma and striking ground will have an energy corresponding to the anode potential. Still further, the ion beam has a direction which is well defined with narrow energy spread (see R2, page 132, lines 24-26).

In contrast to ion beams from an ion source, Appellant respectfully submits that for the particle beam generated from plasma sputtering systems, the background gas pressure is significantly higher than that of the ion beam. In particular, the gas pressure of the sputtering system usually ranges from a few millitorr to about 100 mTorr (see R1, page 12, lines 37-38). In some cases, Appellant respectfully submits that the gas pressure can even be the same as atmosphere for daily applications rather than the utilization in a vacuum chamber. Appellant respectfully further submits that in this range of gas pressure, the collisions between the ions and gas molecules will occur constantly. As a result of the collisions, the energy and direction of the ions will be different from the original values they were when accelerated by the electric field. Still further, there is no focus system in plasma sputtering systems and therefore they are simpler than ion beams and less costly. Also and as a result, the particle beam generated from plasma sputtering systems has a direction poorly defined with wide energy spread and is quite different from that of an ion beam generated from ion guns.

With the above in mind, Appellant respectfully submits that the direction of the ions in a single particle beam from plasma sputtering are random, while the direction of the ions in an ion beam from an ion gun are well defined. Also, the energy of the ions in a single particle beam from plasma sputtering is widely distributed while the energy of ions in an ion beam from ion guns is the same. Accordingly, Appellant respectfully submits that the properties of the two types of particle beams are quite different. As a result, Appellant respectfully submits that since the energy distribution of the plasma sputtering is widely distributed, the smoothness of the material surface can be more easily achieved. In contrast thereto, the focus tight high energy ion beam from ion guns has a tendency to cause an uneven surface because small areas of the surface are impacted with the high energy beam at a time.

In addition to the above, Appellant respectfully submits that the average number of atoms ejected from the target per incident ion is called the sputtering yield. Sputtering yield depends on the ion incident angle, which can be both calculated from theory (see R1, page 177, Fig. 5.2) and measured (see R2, page 2, Fig. 1.1). Still further, there is a maximum sputtering yield which can be achieved at a certain incident angle to the surface normal and the sputtering yield will be lower when the incident angle is some other value. Accordingly, when the target (processed material) surface is rough, the local normal directions of the different zones of the target surface are obviously different from each other. In this case, the sputtering yields of different zones of the target surfaces are not equal if the incident ions come from the same direction. However, if the directions of the ions are poorly defined, the sputtering yields of the different zones of the target surface can be uniform. Therefore, since plasma sputtering creates ions from different directions, it is easier to create a uniform surface with a particle beam generated by plasma sputtering.

In addition, Appellant respectfully submits there will be a shadow of sharp asperities where a well defined ion beam from an ion gun is not able to reach (see R2, page 233, Fig. 6.10). However, this problem can be handled when the ion directions of the particle beam from the plasma sputtering are poorly defined. Because the directions of the ions in the particle beam from plasma sputtering are random, the shadow from one incident direction can be reached by the ions in other directions. Therefore, the particle beam of plasma sputtering has the effect of smoothing the rough surface better than ion beams of ion guns.

Still further to the above, Appellant respectfully submits that the same things happen as described above in cases of changing the microstructure or internal defects of the target

because of the same reasons. In particular, the particle beam of plasma sputtering has better effect than the ion beam from ion guns. The more uniform arrival of ion density can be achieved with less shadow with the plasma sputtering since the ion directions of the particle beam from plasma sputtering are poorly defined.

From the above, Appellant respectfully submits that the advantages of ion beams coming from ion guns include small divergence angle, small energy distribution, individual and separate controlling energy and beam flow with the energies and the directions of the particles being concentrated. However, Appellant respectfully submits that these advantages of ion beams are not suitable for surface modification of a pre-formed material, especially not suitable for the modification of rough surfaces. As a result, Appellant respectfully submits that the disadvantages perceived by some of the particle beam from plasma sputtering being poorly defined and random, are in fact advantages since they are able to process a material surface to be smoother and more uniform than an ion beam.

By way of example, Appellant respectfully submits that an ion beam from an ion gun functions substantially the same as the bullets from a machine gun, whereas the particle beam from plasma sputtering functions similar to the bullets from a scatter gun. Clearly the bullets between these two types of guns are different in that the direction of the bullets from a scatter gun are rather random and therefore hit a large area, while the direction of the bullets from a machine gun are defined to form a line. As a result of the differences between a scatter gun and a machine gun, each is utilized for a particular purpose and cannot achieve the other's.

Based upon the discussion above, Appellant respectfully submits that the advantages remain in bombarding a high temperature superconductor, which cannot be produced with a particle beam produced by the apparatuses of the prior art. In particular, the advantages of a particle beam from plasma sputtering in fabricating and modifying a high temperature superconductor are as follows:

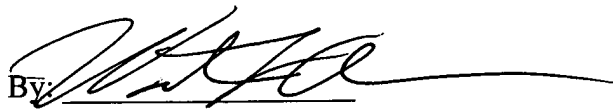
1. The structure of YBCO high temperature superconductors consist of many layers, including the substrate, buffer layers and YBCO superconductor layer. The substrate and buffer layers need to be cleaned, smooth and activated by the particle beams before the fabrication of an upper layer. Since the particle beam from sputtering is distributed in energy and arrives from random directions, smoothing and cleaning can be easily achieved. Still further, since the particle beam from plasma sputtering bombards a larger area, the modification speed is increased.

2. In the process of modifying the YBCO superconductor surface, the oxygen pressure should be high enough to prevent the degrading of the superconductivity. Appellant respectfully submits that a high gas pressure is not suitable for ion beams from ion guns as is discussed above and oxygen is usually harmful to the ion guns. In contrast thereto, a particle beam from plasma sputtering can function in such an atmosphere and can modify the surface of the superconductor device without degrading its superconductivity.

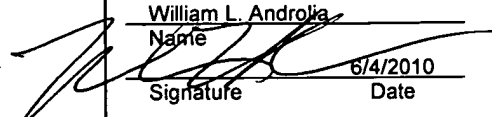
In view of the above, therefore, Appellant respectfully submits that ion beams are not substantially similar to particle beams from plasma sputtering and do not result in a substantially similar process. In addition, Appellant respectfully submits that in a method for surface modification in manufacturing high temperature superconducting devices, a particle beam from plasma sputtering has advantages over ion beams and provides a method utilizing a substantially simpler apparatus which can achieve the processing in less time. Therefore, Appellant respectfully submits that Appellant's invention as claimed by Appellant's claims 1 through 13 and 15 through 18 are not anticipated by nor obvious over the art cited by the Examiner.

Therefore, Appellant respectfully requests that the board favorably consider Appellant's remarks and find Appellant's invention as claimed patentably distinct from the art cited by the Examiner.

Respectfully submitted,

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BEAM MODIFICATION OF MATERIALS,1

ION BOMBARDMENT MODIFICATION OF SURFACES

Fundamentals and Applications

edited by



20149331N

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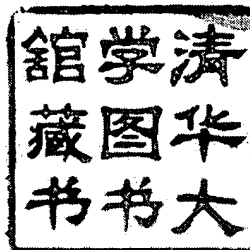
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Chapter 1

HISTORICAL OVERVIEW OF ION-INDUCED MORPHOLOGICAL MODIFICATION OF SURFACES

ORLANDO AUCIELLO

1.1 INTRODUCTION

This book is concerned with ion-bombardment modification of surfaces due mainly to erosional and depositional phenomena. Chemical, electrical, mechanical, etc. changes, due to ion bombardment of surfaces, are the subject of other reviews.

The two most important phenomena relating to ion bombardment modification of surfaces are sputtering and ion implantation. In spite of their similar degree of relevance, the evolution in the understanding of the underlying mechanisms has been quite different. Sputtering was observed by Grove, apparently for the first time, in 1853 (1) as the cause of metallic deposits on the glass walls of discharge tubes. However, it took almost half a century before sputtering was recognised (2) to be an effect caused by positive ions, from the discharge, hitting the cathode; and about a century before a quantitative description of this phenomenon started to be developed. By contrast, it can be said that the evolution in the understanding of the ion implantation process started with the theoretical works of Bohr (3) and Lindhard, Scharff, and Schiøtt (4), who set the bases for the understanding of the stopping power of high and low energy ions penetrating through matter. These works, supported by the first accurate experiments on ion ranges by Davies and coworkers (5, 6), initiated a comparatively faster development, with respect to sputtering, in ion implantation.

A historical overview of the main advances in the understanding of ion bombardment modification of surfaces, due to erosional and depositional phenomena is presented in this chapter. It will be followed by three chapters of a general nature, regarding the subject treated in this book (Chapters 2-4), four more on the fundamentals of surface modification (Chapters 5-8), and finally five on applications of modified surfaces (Chapters 9-13).

1.2 EROSION-INDUCED MORPHOLOGICAL CHANGES

Solid surfaces are generally eroded when bombarded with energetic particles, namely neutral atoms/molecules, ions, electrons, or photons. The phenomenon responsible for such erosion is sputtering, which, according to the present knowledge (see Chapter 2 of this book), presents several variants now known as collisional, thermal, electronic, and explosional sputtering. It can also be understood within the framework of two main concepts, physical and chemical sputtering. The former involves the transfer of kinetic energy from the incident particle to target atoms, which results in the ejection of atoms through the surface. The second is due to a chemical reaction between the impinging particles and target atoms, which leads to the formation of volatile molecules. Details about physical sputtering, from

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both the theoretical and experimental point of view, can be found in a recent comprehensive treatment of this subject (7). Chemical sputtering is also reviewed in ref. (7), Chapter 2 of this book, and in more recent work, related to fusion technology, by Auciello, Stangeby and Haasz (8, 9, 10), who have clarified previous experimental and conceptual inconsistencies, and discovered new aspects of the chemical sputtering phenomenon for carbonaceous materials.

It has been observed that both sputtering mechanisms mentioned above can produce morphological changes on surfaces. Changes induced by physical sputtering arise mainly due to the dependence of the sputtering yield (Y) on the angle of incidence (θ) of the primary beam with respect to the surface (Fig. 1.1). Such a dependence was first observed by Fetz (11), and confirmed later by other groups (12-14). It is important to notice that one reason for the lack of reproducibility in the data of Fig. 1.1 may be the influence of surface topography developed on bombarded surfaces during sputtering yield measurements, an effect to which no appropriate attention has been paid by the different groups.

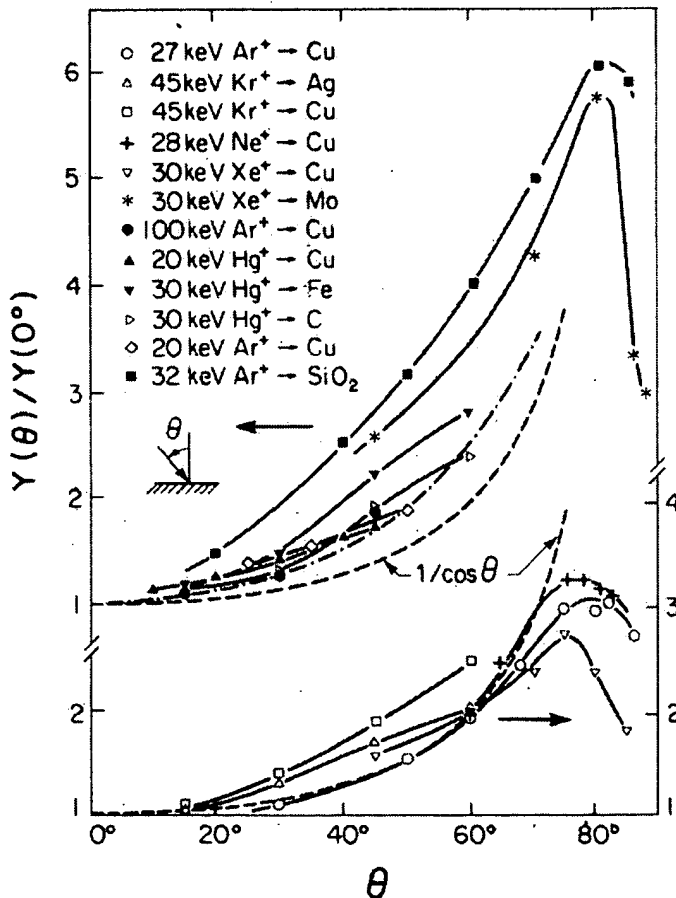


Fig. 1.1. Heavy-ion sputtering yields as a function of angle of incidence (θ). The dash-and-dot curve represents theoretical calculations by Sigmund (7). The solid curves are drawn only to guide the eye.

4.2 DEPOSITION METHODS INVOLVING ION BOMBARDMENT

4.2.1. Radio-frequency bias sputtering

Many of the effects of ion bombardment during deposition were demonstrated using radio-frequency (rf) bias sputtering and later observed in other deposition systems. The equipment and principles of rf sputtering are thoroughly described elsewhere [1] and the technique will only be described here to bring out the capability for ion bombardment during film growth.

An rf diode sputtering system is shown schematically in Fig. 4.1. The target electrode (cathode) is driven by rf power to sustain a glow discharge plasma in the process gas. The cathode develops a negative dc voltage equal to about half the rf peak-to-peak voltage. Ions are accelerated across the cathode dark space to sputter atoms from the target surface. At a typical pressure of 4 Pa (30 mTorr), the sputtered atoms rapidly lose their ejection energy by collisions with the background gas [2], and diffuse to the substrates at essentially thermal energy. Ion bombardment of the substrates is provided by an rf bias voltage applied to the substrate electrode (anode), which develops a negative bias relative to the glow discharge. This potential difference accelerates ions from the plasma to the substrate, providing ion bombardment of the film during deposition. An applied substrate bias of -50 to -300 V is typically used with target voltages of -1000 to -3000V. Other energetic particles striking the growing film are: discharge ions reflected from the target as neutrals; secondary electrons accelerated from the target across the dark space; negative ions emitted from the target [3]; and charge exchange neutrals formed in the anode dark space [4]. Due to the charge exchange process in the anode dark space, very few discharge ions strike the substrate with the full bias voltage, but rather a broad, low energy distribution of ions and neutrals bombards the growing film [4]. Another complication is the lack of direct control over the plasma potential, which is positive with respect to the grounded chamber walls, and depends on the system geometry and gas pressure, typically 20 V at 4 Pa [5]. This plasma potential must be added to the applied substrate bias to determine the maximum ion energy striking the film.

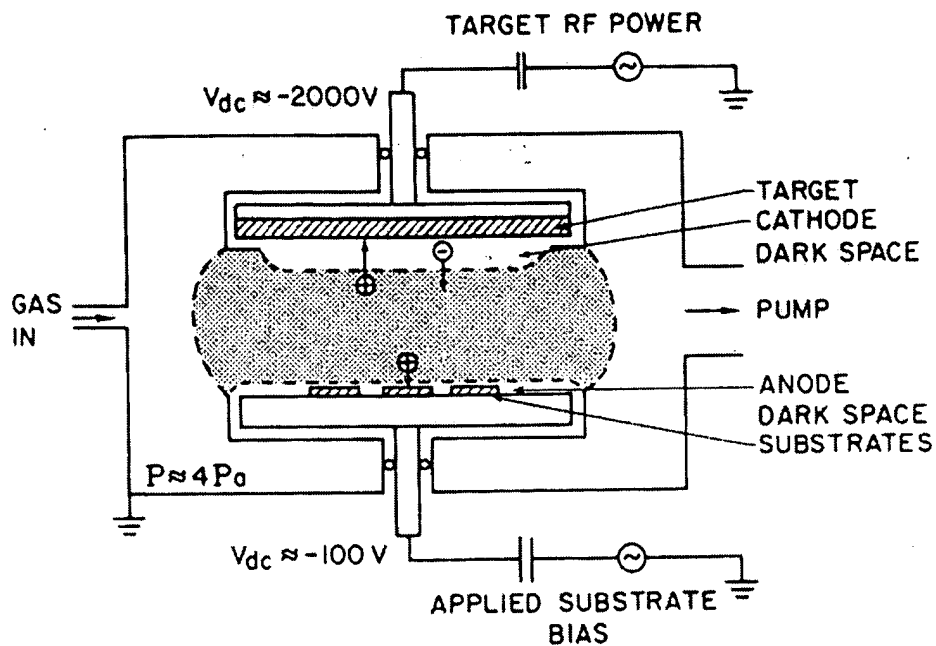


Fig. 4.1. Radio frequency (rf) diode sputtering system for thin film deposition. The dotted region is the discharge plasma.

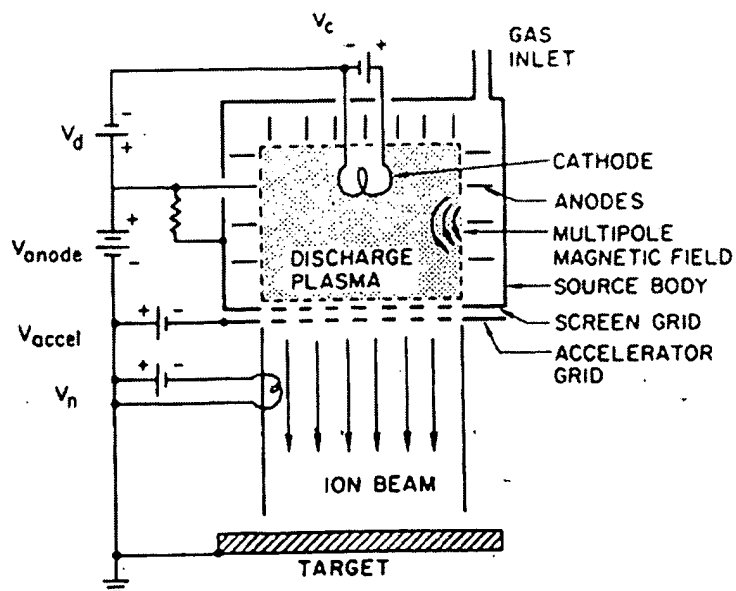


Fig. 4.2. Broad-beam multiaperture ion beam source [9].

Controlling the flux of ions bombarding the film in an rf diode system is not straightforward. Increasing the substrate bias voltage not only increases the bombarding ion energy, but also enhances the ion density in the glow discharge, thereby increasing the ion flux to the substrate. For this reason, the bombarding ion energy and flux are not independent parameters. Cuomo and Gambino [6] have successfully modeled the substrate ion flux as proportional to the one-half power of substrate bias voltage.

$$j \propto V_b^{1/2} \quad (1)$$

but to obtain quantitative flux values requires a detailed accounting of the geometry of the system. This difficulty, together with the broad energy distribution of particles striking the film, has limited the quantitative understanding of substrate bias effects, and the ability to translate data from one system to another.

4.2.2. Broad-beam ion sources

The broad-beam multiaperture electron bombardment ion source was invented in 1961 as an ion thruster for space propulsion [7]. An extensive effort followed to improve the efficiency of this ion source with the goal of obtaining the highest ion beam flux for a given gas flow and power input. These developments have yielded an ion source suitable for material processing, generating collimated, well-characterized ion beams from a wide choice of gas species [8]. The primary advantage of ion beam processing of materials lies in the control available with an ion beam as compared to other plasma processes. The ion flux and ion energy are easily measured and independently controlled, and the direction of ion impact on surfaces is controlled, since the beams operate in a low background gas pressure of typically 0.01 Pa ($\sim 10^{-4}$ Torr). The development of broad-beam ion sources and their applications to etching, surface compound layer formation, and thin film deposition are described in recent review articles [9]. The basic configuration of a broad-beam ion source is shown in Fig. 4.2, which illustrates a cylindrical unit generating a circular beam. The ion source is mounted in a vacuum chamber (not shown) capable of maintaining a background pressure of about 0.01 Pa ($\sim 10^{-4}$ Torr) at the operating conditions (generally a pumping speed of several hundred to several thousand

For many materials applications, a high ion flux is desired in order to carry out the etching/deposition process at a reasonable rate. For reference, 1 mA/cm^2 represents several monolayers equivalent of bombardment per second, and 10^{-4} Pa ($\sim 10^{-6} \text{ Torr}$) represents about one monolayer equivalent of background gas arrival rate per second. Therefore an ion flux of tenths of a mA/cm^2 or higher is necessary for surface treatment processes to occur at a rate exceeding the arrival rate of residual gases, for processing systems with base pressures of 10^{-5} Pa ($\sim 10^{-7} \text{ Torr}$). Also, many applications require low ion energy (several hundred eV or less) to minimize damage to substrates. This combination of high ion flux at low energy is difficult to achieve with the conventional dual grid ion source of Fig. 4.2 because the ion flux is space charge limited by the grid separation. The maximum ion flux is determined by Child's Law [9,10]:

$$j_{\text{max}} = (4\epsilon_0/9)(2e/m)^{1/2} V^{3/2}/l^2, \quad (2)$$

where j_{max} is the maximum ion flux flowing between two planes, V is the potential difference between the planes, l is the spacing between the planes, e/m is the charge-to-mass ratio of the ions, and ϵ_0 is the permittivity of space. For practical ion source configurations, l is approximately given by the spacing between the screen and accelerator grids [9]. This space charge limit sets a ceiling on the ion flux obtainable at a given ion energy, and becomes a severe limit at low energy. For example, with a dual grid system which produces 1.5 mA/cm^2 at 1000 eV ion energy, the ion flux available at 100 eV follows from Eq. 2 as only 0.05 mA/cm^2 . Several improvements in the low energy performance have been made and recently described [9,11].

The output of a broad-beam ion source is an ion beam of well-defined direction and low energy spread. Beam divergence angles can be as low as several degrees, and energy spreads are typically 10 eV [9]. In addition to the ion flux, a substantial neutral gas flow passes through the extraction grid system, since the grids have a high fraction of open area (50-60%). For many materials applications, however, this background gas flux does not greatly affect the process, as the gas is usually an inert or molecular species of low chemical reactivity. The background pressure is

very low (0.01 Pa , $\sim 10^{-4} \text{ Torr}$) compared to a typical rf sputtering or etching plasma ($1\text{-}10 \text{ Pa}$, $\sim 10\text{-}100 \text{ mTorr}$).

This low pressure, combined with the short ion acceleration distance between the grids (about 1 mm), is responsible for the low energy spread. Other species present in the beam include: low energy electrons with a Maxwellian temperature of several eV [8]; charge exchange neutrals caused by collisions of positive beam ions with background gas atoms [12]; and sputtered atoms from the target surface bombarded by the ion beam. Therefore, the ion beam processing environment is characterized by an ion flux of well-defined intensity, energy and direction, with relatively low power input to the substrate from other energetic species. This situation creates a suitable environment for quantitative materials processing by controlled ion bombardment.

The two main configurations for using broad beam ion sources for ion bombardment during film deposition are shown in Figs. 4.3 and 4.4. In the dual ion beam system (Fig. 4.3), an inert or reactive ion beam sputters a target material to produce a deposition flux of atoms onto the substrate. Simultaneously, a second ion source aimed at the substrate supplies an ion beam of inert or reactive ions to bombard the growing film. In the example shown, the substrate holder is equipped with a crystal rate monitor and an ion current monitor to measure the incident atom and ion fluxes directly. These features provide a proper characterization of the incident particle flux onto the film surface. In the second configuration (Fig. 4.4), an ion source is used in conjunction with a vapor source, such as an electron beam evaporator, to add ion bombardment capability to another widely used deposition technique. This configuration is sometimes referred to as "ion assisted deposition". Here also the energy, flux and direction of the bombarding ions are fully characterized and independent of the vapor source. This configuration has also been applied in the technique of molecular beam epitaxy (MBE) with simultaneous ion beam doping, although broad-beam ion sources are not generally used in MBE. In both of these configurations, the arrival flux of atoms and the ion bombardment have different angles of incidence on the substrate. This can cause anisotropic properties in the film plane and may require rotation of the substrate if isotropy in the plane is required.

the x axis is given by $\cos \alpha = p_1 c(y)$ and thus $p_1 = \frac{\cos \alpha}{c(y)} = \text{constant}$.

If in two neighbouring horizontal strata the wave speeds are $c(y_1)$ and $c(y_2)$, then from the constancy of p_1 it is readily observed that, at the interface

$$\frac{\cos \alpha_1}{\cos \alpha_2} = \frac{c(y_1)}{c(y_2)} \quad (34)$$

which is Snell's law in optics.

To conclude this part of the discussion it is to be noted that a reasonably detailed account of general wave front propagation and the role of characteristic equations in following this propagation has been given. In the next section it will be shown how sputter erosion (and other surface modifying processes) is a specific example of such propagation and, consequently, how the morphological development of sputter eroded surface can be predicted from the general techniques just examined. Moreover it will be shown that the several situations discussed above each have their analogues in the sputter erosion area and that the historical developments outlined in the first section can be fully described by general wave propagation formalisms. Given this underlying unified approach some problems, not previously addressed in sputter erosion theory, can be tackled and these potential applications are outlined later in the chapter.

5.4 SPUTTER EROSION AND OTHER SURFACE MODIFICATION PROCESSES

The fundamental processes of sputtering have been fully considered in Section 5.1 and here we will merely use some of the major results of that discussion.

Thus, we note that for an elemental crystalline target of surface orientation (hkl) irradiated at temperature T with atoms of energy E and mass M , incident at a polar angle θ to the surface normal and at azimuthal angle ϕ (defined with respect to a selected crystalline direction) the total sputtering yield Y in atoms ejected per ion must be written as $Y((h,k,l), T, E, M, \theta, \phi)$ for that target material. Further complexity results if one is interested in the double differential yield $\frac{d^2 Y}{dE d\Omega}$ for atoms ejected with energies in the range (E', dE') and over a specified solid angle $d\Omega$.

For initial simplification however we may consider the case of a random (amorphous) target irradiated at fixed temperature with monoenergetic ions of a single species. In this case, all but the dependence upon the polar angle θ vanishes and $Y = Y(\theta)$. A typical form for $Y(\theta)$ is shown schematically in figure 5.2, which reveals that in general $Y(\theta)$ increases from a minimum for $\theta = 0$ (normal incidence) to a maximum, via a relation somewhat like $Y(\theta) = Y(0) \sec^{-n} \theta$, to a maximum at $\theta = \pm \theta_p$ and then declines rather rapidly towards zero as $\theta \rightarrow \pm \pi/2$ (grazing incidence).

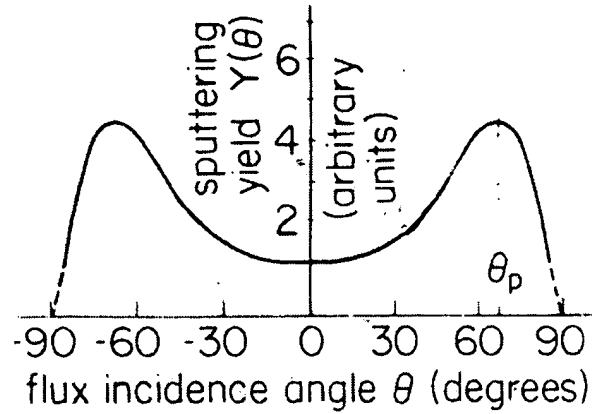


Fig. 5.2 Typical dependence of sputtering yield $Y(\theta)$ with flux incidence angle to surface normal.

If again, for simplification, we consider the case of irradiation by a uniform ion flux density J (ions.cm⁻²sec⁻¹) incident in the $-Oz$ direction on to a surface plane inclined at angle θ to the xOy plane, then the ion flux falling upon unit area of this plane is $J \cos \theta$. The rate of atomic sputtering is thus $J \cdot Y(\theta) \cos \theta$ since the ion flux J makes an angle θ to the surface normal. The linear rate of surface erosion, for a substrate of atomic density N is thus

$$\rho_n = \frac{JY(\theta)\cos\theta}{N} \quad (35)$$

By definition, since atoms are ejected in an averaged model of sputtering, from the surface atomic plane, the erosion process occurs normal to the surface. thus, equation (35) displays the speed of recession of a surface point along the normal direction.

In general the ion flux J may be spatially non-uniform, distributed in direction and variable in time. Thus the differential erosion rate must be written

$$d\rho_n = \frac{J(x,y,z,t)d\omega Y(\theta)\cos\theta}{N} \quad (36a)$$

where $J(x,y,z,t)$ is the partial instantaneous ion flux incident in a solid angle $d\omega$ about the incidence direction θ .

The total erosion rate ρ_n thus

$$\rho_n = \int_{-\pi/2}^{+\pi/2} \frac{J(x,y,z,t) Y(\theta)\cos\theta}{N} d\omega \quad (36b)$$

where the limits to the integral indicate that only ions incident to a surface point from the hemisphere above the surface point may be counted.

Equation (36b) not only accounts for a general surface where all surface points are accessible to the distributed ion flux but also for surface contours where elevated regions

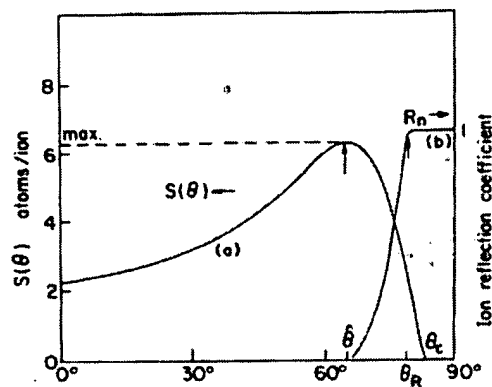


Fig. 6.9 General shape of the functional dependence of (a) the sputtering yield S with respect to θ (angle of incidence of the ion beam with respect to the surface normal); and (b) ion reflection coefficient R_n vs. θ . Three characteristic angles are indicated (see text) (O. Auciello (26)).

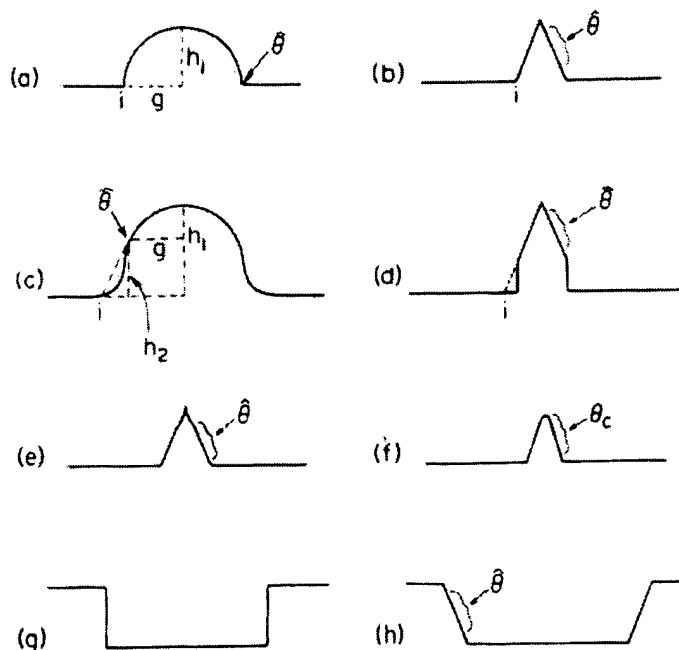


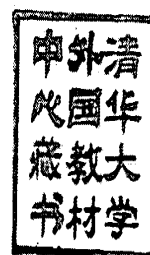
Fig. 6.10 Sketches relevant to the bombardment-induced evolution of asperities and depressions. (a) An asperity of width g and height h_1 which is everywhere convex-up and has a basal slope θ . (b) The pyramid into which (a) would evolve if intersection i moved sufficiently far. (c) A more generalized feature which is convex-up at its center and passes through a slope θ at some intermediate width g and height h_2 . (d) A possible intermediate stage of the bombardment-induced evolution of (c). (e) A pyramid which has a rounded tip, again due to an appropriate fluctuation. (g) A depression with vertical slopes such as is encountered during the fabrication of microcircuitry. (h) The steady-state form of a depression which results owing to appropriate fluctuations in the sputtering process. (Kelly and Auciello (17)).

THIN FILM PROCESSES

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Contents

List of Contributors
Preface

ix
xi

Part I

I-1 Introduction

J. L. Vossen

References

5

Part II PHYSICAL METHODS OF FILM DEPOSITION

II-1 Glow Discharge Sputter Deposition

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I. Introduction	12
II. Physical and Chemical Effects of Ion Bombardment on Surfaces	14
III. Glow Discharges	24
IV. Equipment Configuration	31
V. Preconditioning of Targets, Substrates, and Systems for Film Deposition.	41
VI. The Sputtering Gas	46
VII. Deposition with Simultaneous Ion Bombardment of the Substrate and Growing Film	50
VIII. Rate and Uniformity of Deposition	61
IX. Conclusion	62
References	62

//-1

Glow Discharge Sputter Deposition

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I. Introduction	12
II. Physical and Chemical Effects of Ion Bombardment on Surfaces	14
A. Emission of Neutral Particles—The Sputtering Yield	14
B. Emission of Other Particles	16
C. Emission of Radiation	20
D. Ion Implantation	20
E. Altered Surface Layers and Diffusion	21
F. Dissociation Processes	22
G. Chemical Sputtering	23
III. Glow Discharges	24
A. DC Glow Discharges	24
B. Low-Frequency AC Glow Discharges	27
C. RF Glow Discharges	27
D. Discharge Supporting Modes	29
IV. Equipment Configuration	31
A. Target Assemblies	31
B. Power Supplies	33
C. Instrumentation and Control	36
D. Substrate Heaters	37
E. Wall Losses	39
F. Shields and Shutters	39
G. Deposition Sources for Bias Sputtering and Ion Plating	39
H. Scale-Up Problems	40
V. Preconditioning of Targets, Substrates, and Systems for Film Deposition	41
A. Target Materials	41

B. Presputtering of Targets	42
C. Sputter Etching of Substrates	42
VI. The Sputtering Gas	46
A. Effects of Gas Species, Pressure, and Flow	46
B. Sources of Gas Contamination	46
C. Getter Sputtering	47
D. Reactive Sputtering	48
VII. Deposition with Simultaneous Ion Bombardment of the Substrate and Growing Film	50
A. Plasma, Floating, and Bias Potentials	50
B. Gas Incorporation and Desorption	58
C. Stoichiometry of Films	60
D. Physical Film Properties	60
VIII. Rate and Uniformity of Deposition	61
IX. Conclusion	62
References	62

I. INTRODUCTION

Over the past 20 years or so there have been numerous reviews of sputtering and sputtering processes for film deposition [1-15]. In this chapter we shall take a somewhat different viewpoint than those of most earlier reviewers. We shall attempt to treat this very complex subject from a process viewpoint. That is, we shall discuss the interactions of the process parameters to expose the many permutations and combinations that are available to control the properties of thin films.

Because there are so many interactions among parameters in sputtering systems, it is impossible to separate them completely. Thus, there are necessary, but regrettable references made to later sections throughout the chapter. In an attempt to minimize any confusion that this may cause, we shall give a brief, simple overview of the subject in this section before going to the more detailed discussions.

Figure 1 represents a greatly simplified cross section of a sputtering system. Typically, the target (a plate of the material to be deposited or the material from which a film is to be synthesized) is connected to a negative voltage supply (dc or rf). The substrate holder faces the target. The holder may be grounded, floating, biased, heated, cooled, or some combination of these. A gas is introduced to provide a medium in which a glow discharge can be initiated and maintained. Gas pressures ranging from a few millitorr to about 100 mTorr are used. The most common sputtering gas is argon.

When the glow discharge is started, positive ions strike the target plate and remove mainly neutral target atoms by momentum transfer, and these

II-1. GLOW DISCHARGE SPUTTER DEPOSITION

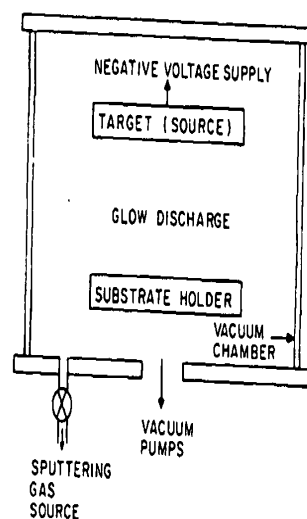


Fig. 1. Simplified cross section of a sputtering system.

condense into thin films. There are, in addition, other particles and radiation produced at the target, all of which may affect film properties (secondary electrons and ions, desorbed gases, x rays, and photons). The electrons and negative ions are accelerated toward the substrate platform and bombard it and the growing film. In some instances, a bias potential (usually negative) is applied to the substrate holder, so that the growing film is subject to positive ion bombardment. This is known variously as *bias sputtering* or *ion plating*. Initially, the term "ion plating" referred to a process in which the deposition source was a thermal evaporation filament instead of a sputtering target and the substrates were connected to a dc sputtering target [16], but it has sometimes been applied to any process in which the substrate is subjected to purposeful ion bombardment during film growth in a glow discharge environment [17].

In some cases, gases or gas mixtures other than Ar are used. Usually this involves some sort of *reactive sputtering* process in which a compound is synthesized by sputtering a metal target (e.g., Ti) in a reactive gas (e.g., O₂ or Ar-O₂ mixtures) to form a compound of the metal and the reactive gas species (e.g., TiO₂). Reactive sputtering is also used to replenish constituents of compound targets lost by dissociation. The reactive version of ion plating is sometimes known as *activated reactive evaporation* [18], but this terminology is more often applied to processes in which an evaporant passes through a glow discharge in transit to an electrically floating or grounded substrate. Reactive sputtering should not be confused with *chemical sputtering* in which the reactive gas (e.g., O₂) reacts with the target surface (e.g., C) to form volatile compounds (e.g.,

CO) that are pumped away [1]. Chemical sputtering is more properly related to ion etching processes (see Chapter V-2).

We shall consider in detail the complex interplay among target kinetics, glow discharge phenomena, substrate conditions, equipment configuration, etc. that bear on the ability to control the properties of thin films.

II. PHYSICAL AND CHEMICAL EFFECTS OF ION BOMBARDMENT ON SURFACES

In sputter deposition, surfaces subject to ion bombardment are usually considered as the source of material from which films are grown. In addition to the neutral (sputtered) material liberated from the bombarded surface which eventually condenses as a film, there are numerous other events that can occur at the target surface which may influence the growth of films profoundly. These include: secondary electron emission, secondary positive and/or negative ion emission, emission of radiation (photons, x rays), reflection of incident particles, heating, chemical dissociation or reaction, bulk diffusion, crystallographic changes, and reflection of some of the emitted particles back to the bombarded surface (backscattering). It should be noted that all of these same phenomena apply to sputter-etching processes (Chapter V-2) in which the workpiece is a sputtering target and to *substrates in most glow discharge deposition processes*. (As will be shown later, any material body immersed in a glow discharge acquires a negative potential with respect to its surroundings and must be considered a sputtering target.)

There have been several recent comprehensive reviews of the kinetics involved when a surface is ion bombarded [3, 6, 8, 12]. Therefore, we shall review them only briefly, emphasizing those target effects that can affect the way in which films grow.

A. Emission of Neutral Particles—The Sputtering Yield

The sputtering yield is defined as the number of atoms ejected from a target surface per incident ion. It is the most fundamental parameter of sputtering processes. Yet all of the surface interaction phenomena involved that contribute to the yield of a given surface are not completely understood. Despite this, an impressive body of literature exists showing the yield to be related to momentum transfer from energetic particles to target surface atoms. There is a threshold for sputtering that is approximately equal to the heat of sublimation. In the energy range of practical interest for sputtering processes (10–5000 eV), the yield increases with

incident ion energy, and with the mass and d-shell filling of the incident ion [19, 20].

The sputtering yield determines the erosion rate of sputtering targets; and largely, but not completely, determines the deposition rate of sputtered films. Several compilations of experimental sputtering yield and related data have been published [3, 5, 6, 21, 22]. All sputtering yields and related data should be used with caution. In glow discharge systems, bombarding ions are by no means monoenergetic, and it is not necessarily valid to use yield values for pure metals when alloys, compounds, or mixtures are sputtered. As will be shown, the sputtering yield of material A from a matrix of A + B is often very different from the sputtering yield of A from a matrix of A. Also, when sputtering yields of compounds are given, dissociation reactions are often ignored. Despite this, tabulations of sputtering yields are useful, if only to give a rough indication of the deposition or etch rate that might be expected for a given material. Tables I–III give a compilation of sputtering yields and relative film deposition

Table I
Sputtering Yield of Elements at 500 eV

Gas	He	Ne	Ar	Kr	Xe	Reference
Element						
Be	0.24	0.42	0.51	0.48	0.35	[23]
C	0.07	—	0.12	0.13	0.17	[23]
Al	0.16	0.73	1.05	0.96	0.82	[23]
Si	0.13	0.48	0.50	0.50	0.42	[23]
Ti	0.07	0.43	0.51	0.48	0.43	[23]
V	0.06	0.48	0.65	0.62	0.63	[23]
Cr	0.17	0.99	1.18	1.39	1.55	[23]
Mn	—	—	—	1.39	1.43	[23]
Mn	—	—	1.90	—	—	[24]
Bi	—	—	6.64	—	—	[24]
Fe	0.15	0.88	1.10	1.07	1.00	[23]
Fe	—	0.63	0.84	0.77	0.88	[25]
Co	0.13	0.90	1.22	1.08	1.08	[23]
Ni	0.16	1.10	1.45	1.30	1.22	[23]
Ni	—	0.99	1.33	1.06	1.22	[25]
Cu	0.24	1.80	2.35	2.35	2.05	[23]
Cu	—	1.35	2.0	1.91	1.91	[25]
Cu (III)	—	2.1	—	2.50	3.9	[26]
Cu	—	—	1.2	—	—	[27]
Ge	0.08	0.68	1.1	1.12	1.04	[23]
Y	0.05	0.46	0.68	0.66	0.48	[23]
Zr	0.02	0.38	0.65	0.51	0.58	[23]

Table I (Continued)

Gas	He	Ne	Ar	Kr	Xe	Reference
Nb	0.03	0.33	0.60	0.55	0.53	[23]
Mo	0.03	0.48	0.80	0.87	0.87	[23]
Mo	—	0.24	0.64	0.59	0.72	[25]
Ru	—	0.57	1.15	1.27	1.20	[23]
Rh	0.06	0.70	1.30	1.43	1.38	[23]
Pd	0.13	1.15	2.08	2.22	2.23	[23]
Ag	0.20	1.77	3.12	3.27	3.32	[23]
Ag	1.0	1.70	2.4	3.1	—	[27]
Ag	—	—	3.06	—	—	[28]
Sm	0.05	0.69	0.80	1.09	1.28	[23]
Gd	0.03	0.48	0.83	1.12	1.20	[23]
Dy	0.03	0.55	0.88	1.15	1.29	[23]
Er	0.03	0.52	0.77	1.07	1.07	[23]
Hf	0.01	0.32	0.70	0.80	—	[23]
Ta	0.01	0.28	0.57	0.87	0.88	[23]
W	0.01	0.28	0.57	0.91	1.01	[23]
Re	0.01	0.37	0.87	1.25	—	[23]
Os	0.01	0.37	0.87	1.27	1.33	[23]
Ir	0.01	0.43	1.01	1.35	1.56	[23]
Pt	0.03	0.63	1.40	1.82	1.93	[23]
Au	0.07	1.08	2.40	3.06	3.01	[23]
Au	0.10	1.3	2.5	—	7.7	[29]
Pb	1.1	—	2.7	—	—	[27]
Th	0.0	0.28	0.62	0.96	1.05	[23]
U	—	0.45	0.85	1.30	0.81	[23]
Sb	—	—	2.83	—	—	[24]
Sn (solid)	—	—	1.2	—	—	[30]
Sn (liquid)	—	—	1.4	—	—	[30]

rates. The latter have been normalized to the sputtering yields of pure metals [21]. All target materials are polycrystalline unless otherwise indicated.

B. Emission of Other Particles

1. Secondary Electrons

Since sputtering targets are held at high negative potentials, secondary electrons are accelerated away from the target surface with an initial energy equal to the target potential. As will be shown in Section III.A, these electrons help to sustain the glow discharge by ionization of neutral sput-

Table II

Sputtering Yield of Elements at 1 keV

Gas	He	N	Ne	N ₂	Ar	Kr	Xe	Reference
Element								
Fe	—	—	0.85	—	1.33	1.42	1.82	[25]
Fe	—	0.55	—	0.78	—	—	—	[3]
Ni	—	—	1.22	—	2.21	1.76	2.26	[25]
Ni	—	0.74	—	1.05	—	—	—	[3]
Ni	—	—	—	—	2.0	2.0	2.0	[26]
Cu	—	—	1.88	—	2.85	3.42	3.6	[25]
Cu	—	1.5	—	—	—	—	—	[3]
Cu	—	—	—	—	3.2	2.5	—	[27]
Cu (111)	—	—	2.75	—	4.5	4.65	6.05	[26]
Cu	—	—	—	1.95	—	—	—	[31]
Mo	—	—	0.49	—	1.13	1.27	1.60	[25]
Mo	—	0.16	—	0.3	—	—	—	[3]
Ag	1.8	—	2.4	—	3.8	4.7	—	[27]
Sn	—	—	—	—	0.8	—	—	[32]
W	—	0.18	—	0.2	—	—	—	[3]
Au	—	—	—	—	1.0	—	—	[32]
Au	0.3	—	2.1	—	4.9	—	—	[29]
Pb	1.5	—	—	—	3.0	—	—	[27]
Sn (liquid)	—	—	—	—	1.7	—	—	[30]
Au (111)	—	—	—	—	3.7	—	—	[33]
Au (100)	—	—	—	—	3.0	—	—	[33]
Au (110)	—	—	—	—	2.0	—	—	[33]
Au	—	—	—	—	3.6	—	—	[33]
Al (111)	—	—	—	—	1.0	—	—	[33]

tering gas atoms which in turn bombard the target and release more secondary electrons in an avalanche process. Upon arrival at the substrate, such energy as they retain after collisions in the gas is liberated in the form of heat [38–43]. Many of the secondary electrons are thermalized by collisions in the gas, but even at high gas pressures, a substantial number of electrons retain full target potential upon impact at the substrates [41, 42].

2. Secondary Ions

Most of the data on ion emission from solids due to primary ion bombardment is to be found in the literature of secondary ion mass spectroscopy (SIMS). Most of this literature deals with the formation and emission of positive ions. However, in glow discharge sputtering, it is highly

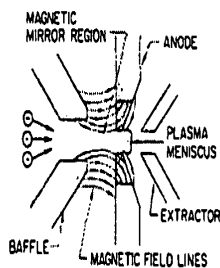


Fig. 6. Anode region of duoplasmatron showing constriction of plasma and plasma meniscus (from Brewer *et al.* [23]).

higher [15, 25] are obtained at about 20 keV beam energy through an aperture of 0.03-cm diameter with an energy spread of 10–50 eV [15]. The converging region of magnetic field lines acts as a magnetic mirror to reflect electrons back to the cathode region [23], enhancing ionization efficiency.

4. Other Ion Sources

Several additional ion source types will be mentioned, with references, to indicate the variety of approaches to generating ions. These are listed with the hope of stimulating novel applications to thin film deposition processes. The *glow discharge* ion source is simply a glow discharge between two plane electrodes with no magnetic field or thermionic cathode. One variation of this configuration is the *hollow anode* ion source in which the beam is extracted through a hole in the cathode plate [26, 27]. The *hollow cathode* ion source, of the same basic type, may be used in place of a thermionic cathode in applications where lifetime or contamination from the cathode are important [4, 28]. The *twin anode* or *electrostatic* ion source uses the geometrical arrangement of the anode surfaces within a surrounding cathode to produce long oscillatory electron trajectories, gaining enhanced ionization with no magnetic field [29].

The term *arc discharge* ion source applies to several configurations. In one type the desired material is vaporized from a crucible directly into a low voltage thermionically supported arc discharge. With some materials the arc is self sustaining with no support gas [30, 31]. No magnetic field is used. Ions are extracted with a low energy spread of 0.1–1.0 eV [31].

The *electrohydrodynamic* ion source [10] is a liquid-metal field-emitting tip which generates a very high brightness, low current ion beam. A strong electric field pulls the liquid into a cusp-shaped tip less than 10^{-4} -cm diameter.

A vapor stream of atoms may be ionized by direct electron bombardment from a hot filament [32]. A variation of this technique, the *ionized cluster* source [33], vaporizes the desired material through a small orifice, inducing cluster formation as the vapor stream expands.

High multiply-charged ion states, for example Ar^{4+} , Kr^{17+} , Xe^{21+} ,

have been obtained by constraining the ions long enough for sequential ionization [34]. *Negative ion* beams may be generated by sputtering the desired material with a beam of low ionization potential material such as cesium [35], and may also be extracted from an off-axis aperture in a duoplasmatron [36]. *Very high current* hydrogen ion beams (several amperes) have been generated with a combined duoplasmatron and Penning ion source [37].

C. Beam Extraction and Control

1. Ion Extraction

Ions in the interior of the plasma diffuse to the plasma boundary, where they are extracted by an electric field. The rate of ion extraction is determined by Child's law of space charge limited current flow [4, 38]. In a planar geometry the space charge limited current density between two planes a distance d apart with potential difference V is

$$j = (4\epsilon_0/9)(2q/m)^{1/2}(V^{3/2}/d^2),$$

where ϵ_0 is the permeability of free space and q/m is the charge-to-mass ratio of the particles. This relationship determines the upper limit for planar current flow and demonstrates two important controls on the current density. Ion extraction from the plasma increases rapidly with increased extraction voltage and with decreased spacing between the plasma boundary and extraction electrode. For nonplanar geometries only the proportionality constant changes in Child's law, thus a given geometry may be characterized by the ratio $j/V^{3/2}$, the *perveance* [4].

Acceleration takes place mainly in the extraction region, since this is usually where the greatest potential drop occurs. However, the ion energy at the target is determined only by the potential difference between the target and the point of origin of the ion, which is usually within a few volts of anode potential. The usual arrangement is to have the target at ground potential and raise the entire source chamber to the desired beam voltage, with the extraction electrode at ground potential or lower.

As an example of extraction geometry, Fig. 7 shows the potential distribution through the extraction region of a Kaufman source [4]. The screen electrode is at the source potential (positive) and the accelerator or extraction electrode is negative. The screen voltage is lower than the anode voltage by the discharge voltage, with the difference between plasma potential and anode voltage not indicated. The extraction electrode is held negative, typically –200 V for source voltage of 1000 V, for two reasons. The rate of ion extraction is increased by a larger potential

The beam profile from a duoplasmatron or other single aperture source is usually close to Gaussian, determined more by the range of transverse velocities and the ion transport optics than by the initial profile at the extractor.

2. Beam Transport

Beam deflection is accomplished by transverse electric fields [42] and mass separation by magnetic fields [43]. If mass separation is desired with a straight trajectory, crossed electric and magnetic fields will select a particular velocity and deflect all others, acting as a mass separator [31, 44].

One type of focusing lens will be mentioned briefly. The Einzel, or unipotential, lens consists of a decelerate section followed by an accelerate section back to the initial beam energy [24]. The field distribution defocuses the beam while it is at high energy and focuses while it is at low energy, resulting in a net focusing of the beam. Examples of using the Einzel lens to focus the beam from a single aperture source are given in Sections III.A and IV.A.

3. Neutralization

The above methods of deflecting and focusing an ion beam apply to a nonneutralized beam. With the broad beam from a Kaufman source, neutralization is necessary to avoid beam spreading by space charge repulsion. This is accomplished by adding electrons from a thermionic filament (Fig. 4) and monitoring the net current to the target or a beam probe. When the net current is zero, the arrival rate of ions equals that of electrons, but the ions are not neutralized by recombination since the mean free path for this process is much larger than the beam diameter [4]. The beam is itself a plasma, in which the electrons rapidly distribute to cancel net charge, thus electron injection does not have to be uniform. The neutralizer filament is sputtered by the beam, and contributes to contamination unless suitable masking is provided. An alternate method of injecting electrons into the beam is from a hollow cathode source (the plasma bridge neutralizer) which may be located outside the beam [4, 44a].

D. System Requirements

1. Materials

Materials in the ion source must be stable at the temperatures involved (several hundred degrees Celsius), have low sputtering yield if subjected to ion bombardment, and low susceptibility to corrosive gases, if used.

Particularly important components are the cathode filaments and electrode apertures. Thermionic cathodes are tantalum or tungsten wire [18], or barium oxide coated mesh [24]. Thermal cycling leads to embrittlement and failure, with exposure to oxygen or more reactive gases shortening filament life greatly. Magnetic fields may be supplied by an external solenoid, usually air cooled, or by permanent magnets, which do not have to be exposed to the plasma. Other surfaces may be molybdenum for thermal stability. In the Kaufman source the screen and accelerator grids span a large diameter, with a small separation, typically 0.1 cm. Thermal expansion leads to distortion, directly affecting extracted ion density and uniformity. These problems are minimized in ion thrusters by using dished molybdenum grids [4], such that thermal distortion occurs uniformly across the grids, but these are difficult to make accurately. Pyrolytic graphite provides the best combination of low thermal expansion, high thermal conductivity, and mechanical stiffness in flat grids [18]. For highest purity films it may be necessary to fabricate parts of the ion source out of materials that are compatible with the desired film [27, 45].

The lifetime of the source is limited by the hot cathode burning out or by buildup of sputtered material in the source, leading to shorting or to insulating coating of electrodes. Flaking of accumulated sputtered material may also cause shorts and insulating supports must be shielded from sputter coating. Lifetimes range from hours to months depending on operating conditions.

2. Vacuum and Gas

The gas pressure in the ion source is determined by the type of source and the ion density needed for the desired ion current. Therefore the pressure at the target is determined by the conductance of the ion source apertures and the pumping speed of the pump, assumed to be in the target region. Background gas in the path of the beam has two effects in addition to the effect of gas pressure on the source itself. Large angle collisions contribute slightly to beam divergence, and charge exchange collisions which result in fast neutrals and slow ions contribute to the sputtering rate at the target without registering as ion current to a probe [18]. The pressure must be below about 1 Pa to sustain a beam without excessive scattering, but is usually maintained around 0.1 Pa or lower to minimize divergence and contamination.

3. Electrical and Other Requirements

The electrical power requirements of the ion sources described above are straightforward. The filaments may be heated with ac or dc current of



21283/931A 3750 PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

ZHENGHE HAN et al.

Serial No.: 10/541,296

Filed: July 6, 2005

For: SURFACE MODIFICATION
METHOD IN FABRICATING HIGH
TEMPERATURE SUPER
CONDUCTIVE DEVICES

Art Unit: 1793

Examiner: Paul A. Wartalowicz

APPELLANT'S RESPONSE

Honorable Commissioner of Patents & Trademarks
P.O. Box 1450
Alexandria VA 22313-1450

Dear Sir:

In response to the Examiner's Answer dated April 5, 2010, submitted herewith are copies of selected portions of "Thin Film Processes", edited by John L. Vossen and Werner Kern and published by the Academic Press, Inc. in New York (R1) and "Ion Bombardment Modification of Surfaces: Fundamentals and Applications", edited by Orlando Auciello and Roger Kelly, published by Elsevier in Amsterdam in 1984 (R2). These two reference documents R1 and R2 will be utilized in Applicant's arguments which are set forth herein below.

Without going into the detail of each and every rejection presented by the Examiner, Appellant respectfully submits that essentially it is the Examiner's opinion, which is not supported by any documentation, that a particle beam generated by a plasma sputtering device is substantially the same as an ion beam, that the properties in the product produced by the utilization of an ion beam would be substantially or inherently the same as that of a plasma sputtering device and the product produced utilizing the plasma sputtering device has no advantages over one produces with an ion beam. Accordingly, it is the Examiner's opinion that Applicant's claims are all anticipated or obvious over the art cited by the Examiner.

In reply to this position by the Examiner, Appellant respectfully submits that a plasma sputtering beam and an ion beam are not equivalent. In particular, each have different properties and Appellant respectfully submits that plasma sputtering has advantages over ion beams. These two issues will be discussed at length below.

In particular, Appellant respectfully submits that for the ion beam generated from ion guns (also called ion sources), a low background gas pressure is usually maintained of about 0.1Pa or lower to minimize divergence of the beam and contamination (see R1, page 187, lines 35 and 36). Since the ion beam operates in a low background gas pressure, the energetic ions will travel a sufficient distance along a free path without collisions with the gas molecules. Therefore, the ion flux and the ion energy are independently controlled and the direction of ion impact on the surfaces is controlled (see R2, page 130, lines 19-23). Also, Appellant respectfully submits that a focus system of the ion source can decrease the divergence of the ion beam. For example, in a normal condition, the plasma edge beside the grid system in ion guns could form a proper shape, which gives the ion beam an initial convergence. Acceleration of the ions takes place mainly in the extraction region in the ion guns, since this is usually where the greatest potential drop occurs (see R1, page 183, lines 24-25). As a result, any ions leaving the discharged plasma and striking ground will have an energy corresponding to the anode potential. Still further, the ion beam has a direction which is well defined with narrow energy spread (see R2, page 132, lines 24-26).

In contrast to ion beams from an ion source, Appellant respectfully submits that for the particle beam generated from plasma sputtering systems, the background gas pressure is significantly higher than that of the ion beam. In particular, the gas pressure of the sputtering system usually ranges from a few millitorr to about 100 mTorr (see R1, page 12, lines 37-38). In some cases, Appellant respectfully submits that the gas pressure can even be the same as atmosphere for daily applications rather than the utilization in a vacuum chamber. Appellant respectfully further submits that in this range of gas pressure, the collisions between the ions and gas molecules will occur constantly. As a result of the collisions, the energy and direction of the ions will be different from the original values they were when accelerated by the electric field. Still further, there is no focus system in plasma sputtering systems and therefore they are simpler than ion beams and less costly. Also and as a result, the particle beam generated from plasma sputtering systems has a direction poorly defined with wide energy spread and is quite different from that of an ion beam generated from ion guns.

With the above in mind, Appellant respectfully submits that the direction of the ions in a single particle beam from plasma sputtering are random, while the direction of the ions in an ion beam from an ion gun are well defined. Also, the energy of the ions in a single particle beam from plasma sputtering is widely distributed while the energy of ions in an ion beam from ion guns is the same. Accordingly, Appellant respectfully submits that the properties of the two types of particle beams are quite different. As a result, Appellant respectfully submits that since the energy distribution of the plasma sputtering is widely distributed, the smoothness of the material surface can be more easily achieved. In contrast thereto, the focus tight high energy ion beam from ion guns has a tendency to cause an uneven surface because small areas of the surface are impacted with the high energy beam at a time.

In addition to the above, Appellant respectfully submits that the average number of atoms ejected from the target per incident ion is called the sputtering yield. Sputtering yield depends on the ion incident angle, which can be both calculated from theory (see R1, page 177, Fig. 5.2) and measured (see R2, page 2, Fig. 1.1). Still further, there is a maximum sputtering yield which can be achieved at a certain incident angle to the surface normal and the sputtering yield will be lower when the incident angle is some other value. Accordingly, when the target (processed material) surface is rough, the local normal directions of the different zones of the target surface are obviously different from each other. In this case, the sputtering yields of different zones of the target surfaces are not equal if the incident ions come from the same direction. However, if the directions of the ions are poorly defined, the sputtering yields of the different zones of the target surface can be uniform. Therefore, since plasma sputtering creates ions from different directions, it is easier to create a uniform surface with a particle beam generated by plasma sputtering.

In addition, Appellant respectfully submits there will be a shadow of sharp asperities where a well defined ion beam from an ion gun is not able to reach (see R2, page 233, Fig. 6.10). However, this problem can be handled when the ion directions of the particle beam from the plasma sputtering are poorly defined. Because the directions of the ions in the particle beam from plasma sputtering are random, the shadow from one incident direction can be reached by the ions in other directions. Therefore, the particle beam of plasma sputtering has the effect of smoothing the rough surface better than ion beams of ion guns.

Still further to the above, Appellant respectfully submits that the same things happen as described above in cases of changing the microstructure or internal defects of the target

because of the same reasons. In particular, the particle beam of plasma sputtering has better effect than the ion beam from ion guns. The more uniform arrival of ion density can be achieved with less shadow with the plasma sputtering since the ion directions of the particle beam from plasma sputtering are poorly defined.

From the above, Appellant respectfully submits that the advantages of ion beams coming from ion guns include small divergence angle, small energy distribution, individual and separate controlling energy and beam flow with the energies and the directions of the particles being concentrated. However, Appellant respectfully submits that these advantages of ion beams are not suitable for surface modification of a pre-formed material, especially not suitable for the modification of rough surfaces. As a result, Appellant respectfully submits that the disadvantages perceived by some of the particle beam from plasma sputtering being poorly defined and random, are in fact advantages since they are able to process a material surface to be smoother and more uniform than an ion beam.

By way of example, Appellant respectfully submits that an ion beam from an ion gun functions substantially the same as the bullets from a machine gun, whereas the particle beam from plasma sputtering functions similar to the bullets from a scatter gun. Clearly the bullets between these two types of guns are different in that the direction of the bullets from a scatter gun are rather random and therefore hit a large area, while the direction of the bullets from a machine gun are defined to form a line. As a result of the differences between a scatter gun and a machine gun, each is utilized for a particular purpose and cannot achieve the other's.

Based upon the discussion above, Appellant respectfully submits that the advantages remain in bombarding a high temperature superconductor, which cannot be produced with a particle beam produced by the apparatuses of the prior art. In particular, the advantages of a particle beam from plasma sputtering in fabricating and modifying a high temperature superconductor are as follows:


1. The structure of YBCO high temperature superconductors consist of many layers, including the substrate, buffer layers and YBCO superconductor layer. The substrate and buffer layers need to be cleaned, smooth and activated by the particle beams before the fabrication of an upper layer. Since the particle beam from sputtering is distributed in energy and arrives from random directions, smoothing and cleaning can be easily achieved. Still further, since the particle beam from plasma sputtering bombards a larger area, the modification speed is increased.

2. In the process of modifying the YBCO superconductor surface, the oxygen pressure should be high enough to prevent the degrading of the superconductivity. Appellant respectfully submits that a high gas pressure is not suitable for ion beams from ion guns as is discussed above and oxygen is usually harmful to the ion guns. In contrast thereto, a particle beam from plasma sputtering can function in such an atmosphere and can modify the surface of the superconductor device without degrading its superconductivity.

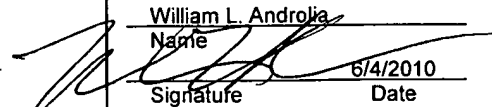
In view of the above, therefore, Appellant respectfully submits that ion beams are not substantially similar to particle beams from plasma sputtering and do not result in a substantially similar process. In addition, Appellant respectfully submits that in a method for surface modification in manufacturing high temperature superconducting devices, a particle beam from plasma sputtering has advantages over ion beams and provides a method utilizing a substantially simpler apparatus which can achieve the processing in less time. Therefore, Appellant respectfully submits that Appellant's invention as claimed by Appellant's claims 1 through 13 and 15 through 18 are not anticipated by nor obvious over the art cited by the Examiner.

Therefore, Appellant respectfully requests that the board favorably consider Appellant's remarks and find Appellant's invention as claimed patentably distinct from the art cited by the Examiner.

Respectfully submitted,

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BEAM MODIFICATION OF MATERIALS,1

ION BOMBARDMENT MODIFICATION OF SURFACES

Fundamentals and Applications

edited by



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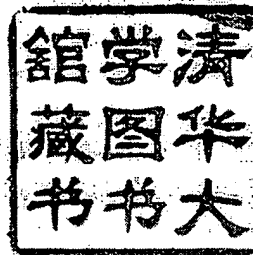
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1

Chapter I

HISTORICAL OVERVIEW OF ION-INDUCED MORPHOLOGICAL MODIFICATION OF SURFACES

ORLANDO AUCIELLO

1.1 INTRODUCTION

This book is concerned with ion-bombardment modification of surfaces due mainly to erosional and depositional phenomena. Chemical, electrical, mechanical, etc. changes, due to ion bombardment of surfaces, are the subject of other reviews.

The two most important phenomena relating to ion bombardment modification of surfaces are sputtering and ion implantation. In spite of their similar degree of relevance, the evolution in the understanding of the underlying mechanisms has been quite different. Sputtering was observed by Grove, apparently for the first time, in 1853 (1) as the cause of metallic deposits on the glass walls of discharge tubes. However, it took almost half a century before sputtering was recognised (2) to be an effect caused by positive ions, from the discharge, hitting the cathode; and about a century before a quantitative description of this phenomenon started to be developed. By contrast, it can be said that the evolution in the understanding of the ion implantation process started with the theoretical works of Bohr (3) and Lindhard, Scharff, and Schiøtt (4), who set the bases for the understanding of the stopping power of high and low energy ions penetrating through matter. These works, supported by the first accurate experiments on ion ranges by Davies and coworkers (5, 6), initiated a comparatively faster development, with respect to sputtering, in ion implantation.

A historical overview of the main advances in the understanding of ion bombardment modification of surfaces, due to erosional and depositional phenomena is presented in this chapter. It will be followed by three chapters of a general nature, regarding the subject treated in this book (Chapters 2-4), four more on the fundamentals of surface modification (Chapters 5-8), and finally five on applications of modified surfaces (Chapters 9-13).

1.2 EROSION-INDUCED MORPHOLOGICAL CHANGES

Solid surfaces are generally eroded when bombarded with energetic particles, namely neutral atoms/molecules, ions, electrons, or photons. The phenomenon responsible for such erosion is sputtering, which, according to the present knowledge (see Chapter 2 of this book), presents several variants now known as collisional, thermal, electronic, and exfoliation sputtering. It can also be understood within the framework of two main concepts, physical and chemical sputtering. The former involves the transfer of kinetic energy from the incident particle to target atoms, which results in the ejection of atoms through the surface. The second is due to a chemical reaction between the impinging particles and target atoms, which leads to the formation of volatile molecules. Details about physical sputtering, from

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both the theoretical and experimental point of view, can be found in a recent comprehensive treatment of this subject (7). Chemical sputtering is also reviewed in ref. (7), Chapter 2 of this book, and in more recent work, related to fusion technology, by Auciello, Stangeby and Haasz (8, 9, 10), who have clarified previous experimental and conceptual inconsistencies, and discovered new aspects of the chemical sputtering phenomenon for carbonaceous materials.

It has been observed that both sputtering mechanisms mentioned above can produce morphological changes on surfaces. Changes induced by physical sputtering arise mainly due to the dependence of the sputtering yield (Y) on the angle of incidence (θ) of the primary beam with respect to the surface (Fig. 1.1). Such a dependence was first observed by Fetzer (11), and confirmed later by other groups (12-14). It is important to notice that one reason for the lack of reproducibility in the data of Fig. 1.1 may be the influence of surface topography developed on bombarded surfaces during sputtering yield measurements, an effect to which no appropriate attention has been paid by the different groups.

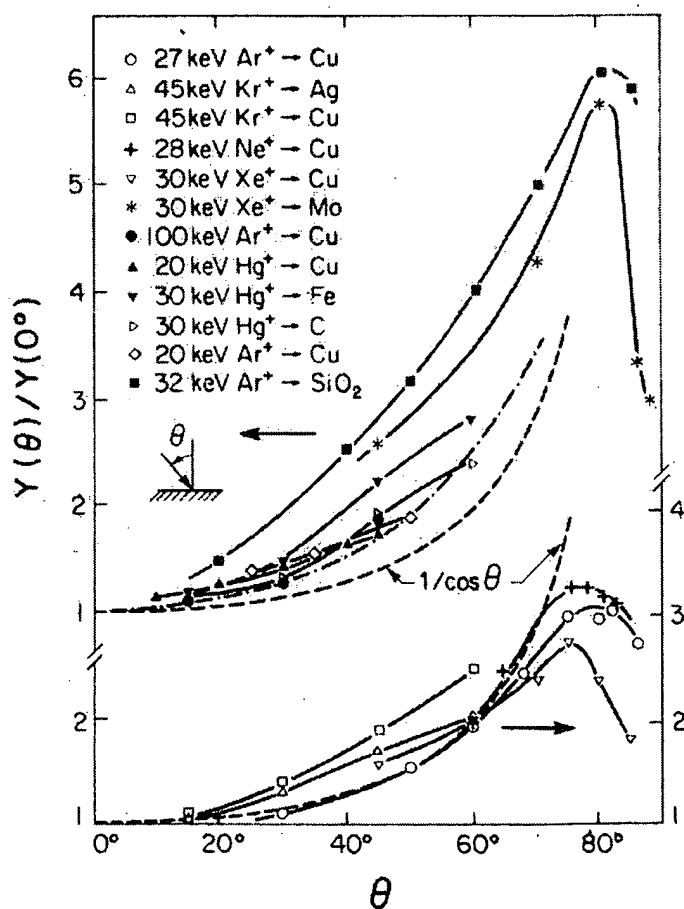


Fig. 1.1. Heavy-ion sputtering yields as a function of angle of incidence (7). The dash-and-dot curve represents theoretical calculations by Sigmund (7). The solid curves are drawn only to guide the eye.

4.2 DEPOSITION METHODS INVOLVING ION BOMBARDMENT

4.2.1. Radio-frequency bias sputtering

Many of the effects of ion bombardment during deposition were demonstrated using radio-frequency (rf) bias sputtering and later observed in other deposition systems. The equipment and principles of rf sputtering are thoroughly described elsewhere [1] and the technique will only be described here to bring out the capability for ion bombardment during film growth.

An rf diode sputtering system is shown schematically in Fig. 4.1. The target electrode (cathode) is driven by rf power to sustain a glow discharge plasma in the process gas. The cathode develops a negative dc voltage equal to about half the rf peak-to-peak voltage. Ions are accelerated across the cathode dark space to sputter atoms from the target surface. At a typical pressure of 4 Pa (30 mTorr), the sputtered atoms rapidly lose their ejection energy by collisions with the background gas [2], and diffuse to the substrates at essentially thermal energy. Ion bombardment of the substrates is provided by an rf bias voltage applied to the substrate electrode (anode), which develops a negative bias relative to the glow discharge. This potential difference accelerates ions from the plasma to the substrate, providing ion bombardment of the film during deposition. An applied substrate bias of -50 to -300 V is typically used with target voltages of -1000 to -3000V. Other energetic particles striking the growing film are: discharge ions reflected from the target as neutrals; secondary electrons accelerated from the target across the dark space; negative ions emitted from the target [3]; and charge exchange neutrals formed in the anode dark space [4]. Due to the charge exchange process in the anode dark space, very few discharge ions strike the substrate with the full bias voltage, but rather a broad, low energy distribution of ions and neutrals bombards the growing film [4]. Another complication is the lack of direct control over the plasma potential, which is positive with respect to the grounded chamber walls, and depends on the system geometry and gas pressure, typically 20 V at 4 Pa [5]. This plasma potential must be added to the applied substrate bias to determine the maximum ion energy striking the film.

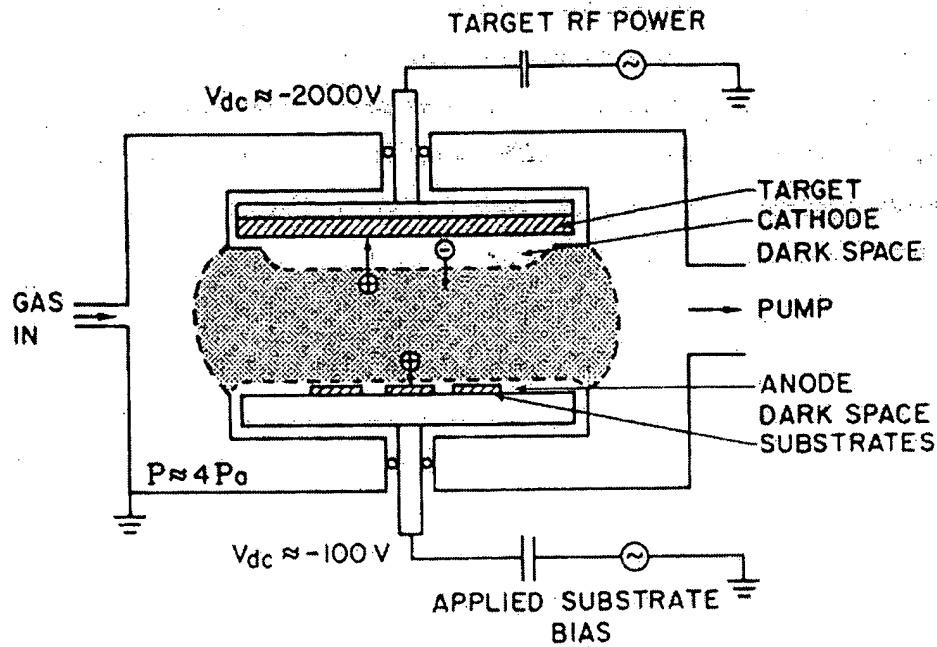


Fig. 4.1. Radio frequency (rf) diode sputtering system for thin film deposition. The dotted region is the discharge plasma.

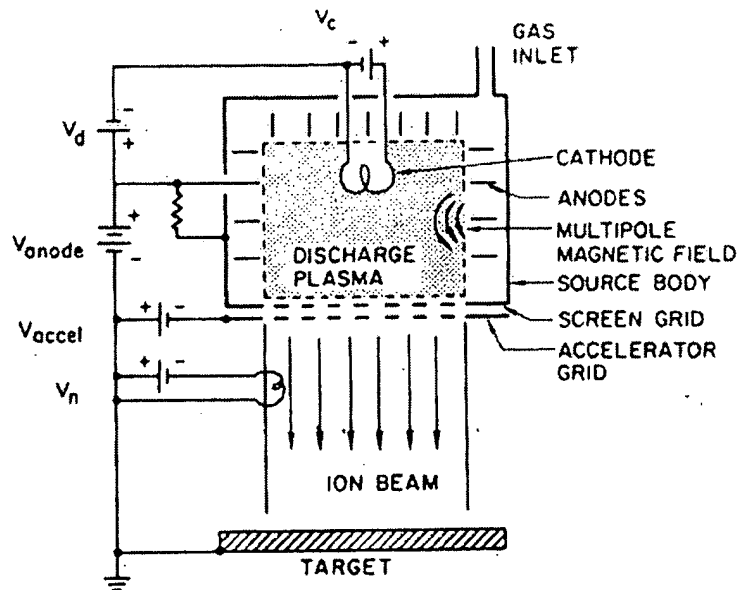


Fig. 4.2. Broad-beam multiperture ion beam source [9].

Controlling the flux of ions bombarding the film in an rf diode system is not straightforward. Increasing the substrate bias voltage not only increases the bombarding ion energy, but also enhances the ion density in the glow discharge, thereby increasing the ion flux to the substrate. For this reason, the bombarding ion energy and flux are not independent parameters. Cuomo and Gambino [6] have successfully modeled the substrate ion flux as proportional to the one-half power of substrate bias voltage,

$$j \propto V_b^{1/2} \quad (1)$$

but to obtain quantitative flux values requires a detailed accounting of the geometry of the system. This difficulty, together with the broad energy distribution of particles striking the film, has limited the quantitative understanding of substrate bias effects, and the ability to translate data from one system to another.

4.2.2. Broad-beam ion sources

The broad-beam multiaperture electron bombardment ion source was invented in 1961 as an ion thruster for space propulsion [7]. An extensive effort followed to improve the efficiency of this ion source with the goal of obtaining the highest ion beam flux for a given gas flow and power input. These developments have yielded an ion source suitable for material processing, generating collimated, well-characterized ion beams from a wide choice of gas species [8]. The primary advantage of ion beam processing of materials lies in the control available with an ion beam as compared to other plasma processes. The ion flux and ion energy are easily measured and independently controlled, and the direction of ion impact on surfaces is controlled, since the beams operate in a low background gas pressure of typically 0.01 Pa ($\sim 10^{-4}$ Torr). The development of broad-beam ion sources and their applications to etching, surface compound layer formation, and thin film deposition are described in recent review articles [9]. The basic configuration of a broad-beam ion source is shown in Fig. 4.2, which illustrates a cylindrical unit generating a circular beam. The ion source is mounted in a vacuum chamber (not shown) capable of maintaining a background pressure of about 0.01 Pa ($\sim 10^{-4}$ Torr) at the operating conditions (generally a pumping speed of several hundred to several thousand

For many materials applications, a high ion flux is desired in order to carry out the etching/deposition process at a reasonable rate. For reference, 1 mA/cm^2 represents several monolayers equivalent of bombardment per second, and 10^{-4} Pa ($\sim 10^{-6} \text{ Torr}$) represents about one monolayer equivalent of background gas arrival rate per second. Therefore an ion flux of tenths of a mA/cm^2 or higher is necessary for surface treatment processes to occur at a rate exceeding the arrival rate of residual gases, for processing systems with base pressures of 10^{-5} Pa ($\sim 10^{-7} \text{ Torr}$). Also, many applications require low ion energy (several hundred eV or less) to minimize damage to substrates. This combination of high ion flux at low energy is difficult to achieve with the conventional dual grid ion source of Fig. 4.2 because the ion flux is space charge limited by the grid separation. The maximum ion flux is determined by Child's Law [9,10]:

$$j_{\text{max}} = (4\epsilon_0/9)(2e/m)^{1/2} V^{3/2}/l^2, \quad (2)$$

where j_{max} is the maximum ion flux flowing between two planes, V is the potential difference between the planes, l is the spacing between the planes, e/m is the charge-to-mass ratio of the ions, and ϵ_0 is the permittivity of space. For practical ion source configurations, l is approximately given by the spacing between the screen and accelerator grids [9]. This space charge limit sets a ceiling on the ion flux obtainable at a given ion energy, and becomes a severe limit at low energy. For example, with a dual grid system which produces 1.5 mA/cm^2 at 1000 eV ion energy, the ion flux available at 100 eV follows from Eq. 2 as only 0.05 mA/cm^2 . Several improvements in the low energy performance have been made and recently described [9,11].

The output of a broad-beam ion source is an ion beam of well-defined direction and low energy spread. Beam divergence angles can be as low as several degrees, and energy spreads are typically 10 eV [9]. In addition to the ion flux, a substantial neutral gas flow passes through the extraction grid system, since the grids have a high fraction of open area (50-60%). For many materials applications, however, this background gas flux does not greatly affect the process, as the gas is usually an inert or molecular species of low chemical reactivity. The background pressure is

very low (0.01 Pa, $\sim 10^{-4}$ Torr) compared to a typical rf sputtering or etching plasma (1-10 Pa, ~ 10 -100 mTorr).

This low pressure, combined with the short ion acceleration distance between the grids (about 1 mm), is responsible for the low energy spread. Other species present in the beam include: low energy electrons with a Maxwellian temperature of several eV [8]; charge exchange neutrals caused by collisions of positive beam ions with background gas atoms [12]; and sputtered atoms from the target surface bombarded by the ion beam. Therefore, the ion beam processing environment is characterized by an ion flux of well-defined intensity, energy and direction, with relatively low power input to the substrate from other energetic species. This situation creates a suitable environment for quantitative materials processing by controlled ion bombardment.

The two main configurations for using broad beam ion sources for ion bombardment during film deposition are shown in Figs. 4.3 and 4.4. In the dual ion beam system (Fig. 4.3), an inert or reactive ion beam sputters a target material to produce a deposition flux of atoms onto the substrate. Simultaneously, a second ion source aimed at the substrate supplies an ion beam of inert or reactive ions to bombard the growing film. In the example shown, the substrate holder is equipped with a crystal rate monitor and an ion current monitor to measure the incident atom and ion fluxes directly. These features provide a proper characterization of the incident particle flux onto the film surface. In the second configuration (Fig. 4.4), an ion source is used in conjunction with a vapor source, such as an electron beam evaporator, to add ion bombardment capability to another widely used deposition technique. This configuration is sometimes referred to as "ion assisted deposition". Here also the energy, flux and direction of the bombarding ions are fully characterized and independent of the vapor source. This configuration has also been applied in the technique of molecular beam epitaxy (MBE) with simultaneous ion beam doping, although broad-beam ion sources are not generally used in MBE. In both of these configurations, the arrival flux of atoms and the ion bombardment have different angles of incidence on the substrate. This can cause anisotropic properties in the film plane and may require rotation of the substrate if isotropy in the plane is required.

the x axis is given by $\cos \alpha = p_1 c(y)$ and thus $p_1 = \frac{\cos \alpha}{c(y)} = \text{constant}$.

If in two neighbouring horizontal strata the wave speeds are $c(y_1)$ and $c(y_2)$, then from the constancy of p_1 it is readily observed that, at the interface

$$\frac{\cos \alpha_1}{\cos \alpha_2} = \frac{c(y_1)}{c(y_2)} \quad (32)$$

which is Snell's law in optics.

To conclude this part of the discussion it is to be noted that a reasonably detailed account of general wave front propagation and the role of characteristic equations in following this propagation has been given. In the next section it will be shown how sputter erosion (and other surface modifying processes) is a specific example of such propagation and, consequently, how the morphological development of sputter eroded surface can be predicted from the general techniques just examined. Moreover it will be shown that the several situations discussed above each have their analogues in the sputter erosion area and that the historical developments outlined in the first section can be fully described by general wave propagation formalisms. Given this underlying unified approach some problems, not previously addressed in sputter erosion theory, can be tackled and these potential applications are outlined later in the chapter.

5.4 SPUTTER EROSION AND OTHER SURFACE MODIFICATION PROCESSES

The fundamental processes of sputtering have been fully considered in Section 5.1 and here we will merely use some of the major results of that discussion.

Thus, we note that for an elemental crystalline target of surface orientation (hkl) irradiated at temperature T with atoms of energy E and mass M , incident at a polar angle θ to the surface normal and at azimuthal angle ϕ (defined with respect to a selected crystalline direction) the total sputtering yield Y in atoms ejected per ion must be written as $Y((h,k,l), T, E, M, \theta, \phi)$ for that target material. Further complexity results if one is interested in the double differential yield $\frac{d^2 Y}{dE d\Omega}$ for atoms ejected with energies in the range (E, dE) and over a specified solid angle $d\Omega$.

For initial simplification however we may consider the case of a random (amorphous) target irradiated at fixed temperature with monoenergetic ions of a single species. In this case, all but the dependence upon the polar angle θ vanishes and $Y = Y(\theta)$. A typical form for $Y(\theta)$ is shown schematically in figure 5.2, which reveals that in general $Y(\theta)$ increases from a minimum for $\theta = 0$ (normal incidence) to a maximum, via a relation somewhat like $Y(\theta) = Y(0) \sec^{-n} \theta$, to a maximum at $\theta = \pm \theta_p$ and then declines rather rapidly towards zero as $\theta \rightarrow \pm \pi/2$ (grazing incidence).

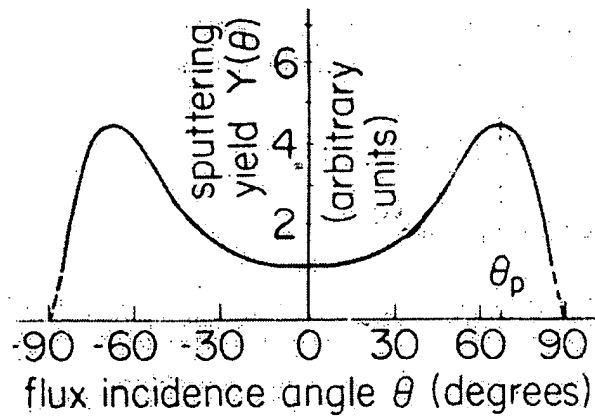


Fig. 5.2 Typical dependence of sputtering yield $Y(\theta)$ with flux incidence angle to surface normal.

If again, for simplification, we consider the case of irradiation by a uniform ion flux density J (ions.cm⁻²sec⁻¹) incident in the $-Oz$ direction on to a surface plane inclined at angle θ to the xOy plane, then the ion flux falling upon unit area of this plane is $J \cos \theta$. The rate of atomic sputtering is thus $J \cdot Y(\theta) \cos \theta$ since the ion flux J makes an angle θ to the surface normal. The linear rate of surface erosion, for a substrate of atomic density N is thus

$$\rho_n = \frac{JY(\theta)\cos\theta}{N} \quad (35)$$

By definition, since atoms are ejected in an averaged model of sputtering, from the surface atomic plane, the erosion process occurs normal to the surface. thus, equation (35) displays the speed of recession of a surface point along the normal direction.

In general the ion flux J may be spatially non-uniform, distributed in direction and variable in time. Thus the differential erosion rate must be written

$$d\rho_n = \frac{J(x,y,z,t)d\omega Y(\theta)\cos\theta}{N} \quad (36a)$$

where $J(x,y,z,t)$ is the partial instantaneous ion flux incident in a solid angle $d\omega$ about the incidence direction θ .

The total erosion rate ρ_n thus

$$\rho_n = \int_{-\pi/2}^{+\pi/2} \frac{J(x,y,z,t) Y(\theta)\cos\theta}{N} d\omega \quad (36b)$$

where the limits to the integral indicate that only ions incident to a surface point from the hemisphere above the surface point may be counted.

Equation (36b) not only accounts for a general surface where all surface points are accessible to the distributed ion flux but also for surface contours where elevated regions

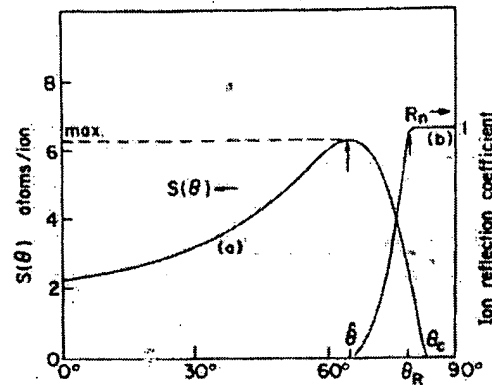


Fig. 6.9 General shape of the functional dependence of (a) the sputtering yield S with respect to θ (angle of incidence of the ion beam with respect to the surface normal); and (b) ion reflection coefficient R_n vs. θ . Three characteristic angles are indicated (see text) (O. Auciello (26)).

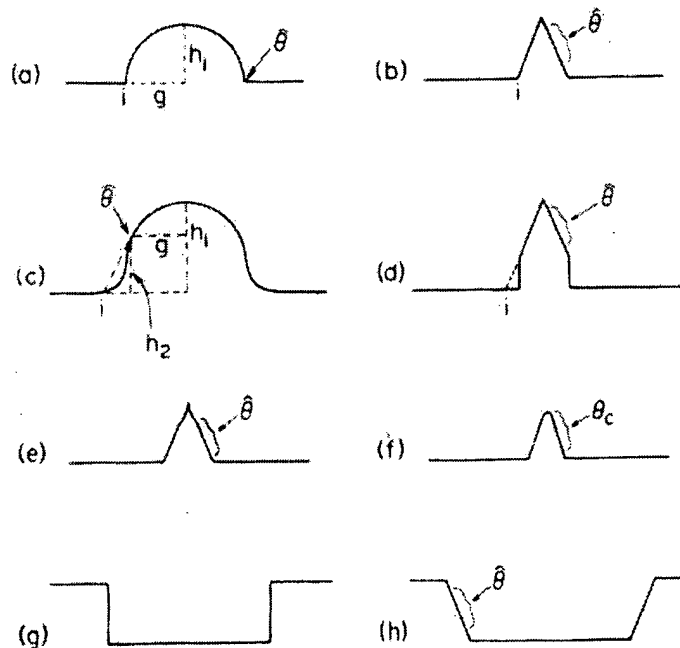


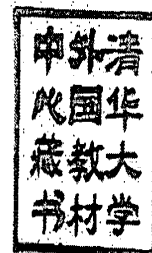
Fig. 6.10 Sketches relevant to the bombardment-induced evolution of asperities and depressions. (a) An asperity of width g and height h_1 which is everywhere convex-up and has a basal slope θ . (b) The pyramid into which (a) would evolve if intersection i moved sufficiently far. (c) A more generalized feature which is convex-up at its center and passes through a slope θ at some intermediate width g and height h_2 . (d) A possible intermediate stage of the bombardment-induced evolution of (c). (e) A pyramid which has a rounded tip, again due to an appropriate fluctuation. (g) A depression with vertical slopes such as is encountered during the fabrication of microcircuitry. (h) The steady-state form of a depression which results owing to appropriate fluctuations in the sputtering process. (Kelly and Auciello (17)).

THIN FILM PROCESSES

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Contents

<i>List of Contributors</i>	ix
<i>Preface</i>	xi

Part I

I-1 Introduction

J. L. Vossen

References	5
------------	---

Part II PHYSICAL METHODS OF FILM DEPOSITION

II-1 Glow Discharge Sputter Deposition

J. L. Vossen and J. J. Cuomo

I. Introduction	12
II. Physical and Chemical Effects of Ion Bombardment on Surfaces	14
III. Glow Discharges	24
IV. Equipment Configuration	31
V. Preconditioning of Targets, Substrates, and Systems for Film Deposition.	41
VI. The Sputtering Gas	46
VII. Deposition with Simultaneous Ion Bombardment of the Substrate and Growing Film	50
VIII. Rate and Uniformity of Deposition	61
IX. Conclusion	62
References	62

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Glow Discharge Sputter Deposition

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I. Introduction	12
II. Physical and Chemical Effects of Ion Bombardment on Surfaces	14
A. Emission of Neutral Particles—The Sputtering Yield	14
B. Emission of Other Particles	16
C. Emission of Radiation	20
D. Ion Implantation	20
E. Altered Surface Layers and Diffusion	21
F. Dissociation Processes	22
G. Chemical Sputtering	23
III. Glow Discharges	24
A. DC Glow Discharges	24
B. Low-Frequency AC Glow Discharges	27
C. RF Glow Discharges	27
D. Discharge Supporting Modes	29
IV. Equipment Configuration	31
A. Target Assemblies	31
B. Power Supplies	33
C. Instrumentation and Control	36
D. Substrate Heaters	37
E. Wall Losses	39
F. Shields and Shutters	39
G. Deposition Sources for Bias Sputtering and Ion Plating	39
H. Scale-Up Problems	40
V. Preconditioning of Targets, Substrates, and Systems for Film Deposition	41
A. Target Materials	41

B. Presputtering of Targets	42
C. Sputter Etching of Substrates	42
VI. The Sputtering Gas	46
A. Effects of Gas Species, Pressure, and Flow	46
B. Sources of Gas Contamination	46
C. Getter Sputtering	47
D. Reactive Sputtering	48
VII. Deposition with Simultaneous Ion Bombardment of the Substrate and Growing Film	50
A. Plasma, Floating, and Bias Potentials	50
B. Gas Incorporation and Desorption	58
C. Stoichiometry of Films	60
D. Physical Film Properties	60
VIII. Rate and Uniformity of Deposition	61
IX. Conclusion	62
References	62

I. INTRODUCTION

Over the past 20 years or so there have been numerous reviews of sputtering and sputtering processes for film deposition [1-15]. In this chapter we shall take a somewhat different viewpoint than those of most earlier reviewers. We shall attempt to treat this very complex subject from a process viewpoint. That is, we shall discuss the interactions of the process parameters to expose the many permutations and combinations that are available to control the properties of thin films.

Because there are so many interactions among parameters in sputtering systems, it is impossible to separate them completely. Thus, there are necessary, but regrettable references made to later sections throughout the chapter. In an attempt to minimize any confusion that this may cause, we shall give a brief, simple overview of the subject in this section before going to the more detailed discussions.

Figure 1 represents a greatly simplified cross section of a sputtering system. Typically, the target (a plate of the material to be deposited or the material from which a film is to be synthesized) is connected to a negative voltage supply (dc or rf). The substrate holder faces the target. The holder may be grounded, floating, biased, heated, cooled, or some combination of these. A gas is introduced to provide a medium in which a glow discharge can be initiated and maintained. Gas pressures ranging from a few millitorr to about 100 mTorr are used. The most common sputtering gas is argon.

When the glow discharge is started, positive ions strike the target plate and remove mainly neutral target atoms by momentum transfer, and these

II-1. GLOW DISCHARGE SPUTTER DEPOSITION

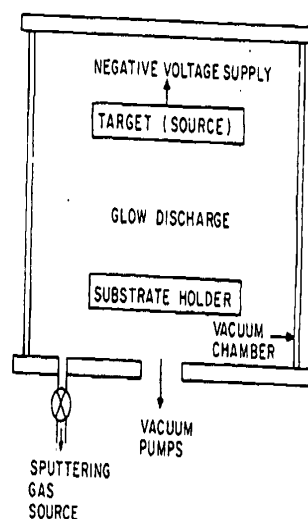


Fig. 1. Simplified cross section of a sputtering system.

condense into thin films. There are, in addition, other particles and radiation produced at the target, all of which may affect film properties (secondary electrons and ions, desorbed gases, x rays, and photons). The electrons and negative ions are accelerated toward the substrate platform and bombard it and the growing film. In some instances, a bias potential (usually negative) is applied to the substrate holder, so that the growing film is subject to positive ion bombardment. This is known variously as *bias sputtering* or *ion plating*. Initially, the term "ion plating" referred to a process in which the deposition source was a thermal evaporation filament instead of a sputtering target and the substrates were connected to a dc sputtering target [16], but it has sometimes been applied to any process in which the substrate is subjected to purposeful ion bombardment during film growth in a glow discharge environment [17].

In some cases, gases or gas mixtures other than Ar are used. Usually this involves some sort of *reactive sputtering* process in which a compound is synthesized by sputtering a metal target (e.g., Ti) in a reactive gas (e.g., O_2 or Ar- O_2 mixtures) to form a compound of the metal and the reactive gas species (e.g., TiO_2). Reactive sputtering is also used to replenish constituents of compound targets lost by dissociation. The reactive version of ion plating is sometimes known as *activated reactive evaporation* [18], but this terminology is more often applied to processes in which an evaporant passes through a glow discharge in transit to an electrically floating or grounded substrate. Reactive sputtering should not be confused with *chemical sputtering* in which the reactive gas (e.g., O_2) reacts with the target surface (e.g., C) to form volatile compounds (e.g.,

CO) that are pumped away [1]. Chemical sputtering is more properly related to ion etching processes (see Chapter V-2).

We shall consider in detail the complex interplay among target kinetics, glow discharge phenomena, substrate conditions, equipment configuration, etc. that bear on the ability to control the properties of thin films.

II. PHYSICAL AND CHEMICAL EFFECTS OF ION BOMBARDMENT ON SURFACES

In sputter deposition, surfaces subject to ion bombardment are usually considered as the source of material from which films are grown. In addition to the neutral (sputtered) material liberated from the bombarded surface which eventually condenses as a film, there are numerous other events that can occur at the target surface which may influence the growth of films profoundly. These include: secondary electron emission, secondary positive and/or negative ion emission, emission of radiation (photons, x rays), reflection of incident particles, heating, chemical dissociation or reaction, bulk diffusion, crystallographic changes, and reflection of some of the emitted particles back to the bombarded surface (backscattering). It should be noted that all of these same phenomena apply to sputter-etching processes (Chapter V-2) in which the workpiece is a sputtering target and to *substrates in most glow discharge deposition processes*. (As will be shown later, any material body immersed in a glow discharge acquires a negative potential with respect to its surroundings and must be considered a sputtering target.)

There have been several recent comprehensive reviews of the kinetics involved when a surface is ion bombarded [3, 6, 8, 12]. Therefore, we shall review them only briefly, emphasizing those target effects that can affect the way in which films grow.

A. Emission of Neutral Particles—The Sputtering Yield

The sputtering yield is defined as the number of atoms ejected from a target surface per incident ion. It is the most fundamental parameter of sputtering processes. Yet all of the surface interaction phenomena involved that contribute to the yield of a given surface are not completely understood. Despite this, an impressive body of literature exists showing the yield to be related to momentum transfer from energetic particles to target surface atoms. There is a threshold for sputtering that is approximately equal to the heat of sublimation. In the energy range of practical interest for sputtering processes (10–5000 eV), the yield increases with

incident ion energy, and with the mass and d-shell filling of the incident ion [19, 20].

The sputtering yield determines the erosion rate of sputtering targets; and largely, but not completely, determines the deposition rate of sputtered films. Several compilations of experimental sputtering yield and related data have been published [3, 5, 6, 21, 22]. All sputtering yields and related data should be used with caution. In glow discharge systems, bombarding ions are by no means monoenergetic, and it is not necessarily valid to use yield values for pure metals when alloys, compounds, or mixtures are sputtered. As will be shown, the sputtering yield of material A from a matrix of A + B is often very different from the sputtering yield of A from a matrix of A. Also, when sputtering yields of compounds are given, dissociation reactions are often ignored. Despite this, tabulations of sputtering yields are useful, if only to give a rough indication of the deposition or etch rate that might be expected for a given material. Tables I–III give a compilation of sputtering yields and relative film deposition

Table I
Sputtering Yield of Elements at 500 eV

Gas	He	Ne	Ar	Kr	Xe	Reference
Element						
Be	0.24	0.42	0.51	0.48	0.35	[23]
C	0.07	—	0.12	0.13	0.17	[23]
Al	0.16	0.73	1.05	0.96	0.82	[23]
Si	0.13	0.48	0.50	0.50	0.42	[23]
Ti	0.07	0.43	0.51	0.48	0.43	[23]
V	0.06	0.48	0.65	0.62	0.63	[23]
Cr	0.17	0.99	1.18	1.39	1.55	[23]
Mn	—	—	—	1.39	1.43	[23]
Mn	—	—	1.90	—	—	[24]
Bi	—	—	6.64	—	—	[24]
Fe	0.15	0.88	1.10	1.07	1.00	[23]
Fe	—	0.63	0.84	0.77	0.88	[25]
Co	0.13	0.90	1.22	1.08	1.08	[23]
Ni	0.16	1.10	1.45	1.30	1.22	[23]
Ni	—	0.99	1.33	1.06	1.22	[25]
Cu	0.24	1.80	2.35	2.35	2.05	[23]
Cu	—	1.35	2.0	1.91	1.91	[25]
Cu (111)	—	2.1	—	2.50	3.9	[26]
Cu	—	—	1.2	—	—	[27]
Ge	0.08	0.68	1.1	1.12	1.04	[23]
Y	0.05	0.46	0.68	0.66	0.48	[23]
Zr	0.02	0.38	0.65	0.51	0.58	[23]

Table I (Continued)

Gas	He	Ne	Ar	Kr	Xe	Reference
Nb	0.03	0.33	0.60	0.55	0.53	[23]
Mo	0.03	0.48	0.80	0.87	0.87	[23]
Mo	—	0.24	0.64	0.59	0.72	[25]
Ru	—	0.57	1.15	1.27	1.20	[23]
Rh	0.06	0.70	1.30	1.43	1.38	[23]
Pd	0.13	1.15	2.08	2.22	2.23	[23]
Ag	0.20	1.77	3.12	3.27	3.32	[23]
Ag	1.0	1.70	2.4	3.1	—	[27]
Ag	—	—	3.06	—	—	[28]
Sm	0.05	0.69	0.80	1.09	1.28	[23]
Gd	0.03	0.48	0.83	1.12	1.20	[23]
Dy	0.03	0.55	0.88	1.15	1.29	[23]
Er	0.03	0.52	0.77	1.07	1.07	[23]
Hf	0.01	0.32	0.70	0.80	—	[23]
Ta	0.01	0.28	0.57	0.87	0.88	[23]
W	0.01	0.28	0.57	0.91	1.01	[23]
Re	0.01	0.37	0.87	1.25	—	[23]
Os	0.01	0.37	0.87	1.27	1.33	[23]
Ir	0.01	0.43	1.01	1.35	1.56	[23]
Pt	0.03	0.63	1.40	1.82	1.93	[23]
Au	0.07	1.08	2.40	3.06	3.01	[23]
Au	0.10	1.3	2.5	—	7.7	[29]
Pb	1.1	—	2.7	—	—	[27]
Th	0.0	0.28	0.62	0.96	1.05	[23]
U	—	0.45	0.85	1.30	0.81	[23]
Sb	—	—	2.83	—	—	[24]
Sn (solid)	—	—	1.2	—	—	[30]
Sn (liquid)	—	—	1.4	—	—	[30]

rates. The latter have been normalized to the sputtering yields of pure metals [21]. All target materials are polycrystalline unless otherwise indicated.

B. Emission of Other Particles

1. Secondary Electrons

Since sputtering targets are held at high negative potentials, secondary electrons are accelerated away from the target surface with an initial energy equal to the target potential. As will be shown in Section III.A, these electrons help to sustain the glow discharge by ionization of neutral sput-

Table II

Sputtering Yield of Elements at 1 keV

Gas	He	N	Ne	N ₂	Ar	Kr	Xe	Reference
Element								
Fe	—	—	0.85	—	1.33	1.42	1.82	[25]
Fe	—	0.55	—	0.78	—	—	—	[3]
Ni	—	—	1.22	—	2.21	1.76	2.26	[25]
Ni	—	0.74	—	1.05	—	—	—	[3]
Ni	—	—	—	—	2.0	2.0	2.0	[26]
Cu	—	—	1.88	—	2.85	3.42	3.6	[25]
Cu	—	1.5	—	—	—	—	—	[3]
Cu	—	—	—	—	3.2	2.5	—	[27]
Cu (111)	—	—	2.75	—	4.5	4.65	6.05	[26]
Cu	—	—	—	1.95	—	—	—	[31]
Mo	—	—	0.49	—	1.13	1.27	1.60	[25]
Mo	—	0.16	—	0.3	—	—	—	[3]
Ag	1.8	—	2.4	—	3.8	4.7	—	[27]
Sn	—	—	—	—	0.8	—	—	[32]
W	—	0.18	—	0.2	—	—	—	[3]
Au	—	—	—	—	1.0	—	—	[32]
Au	0.3	—	2.1	—	4.9	—	—	[29]
Pb	1.5	—	—	—	3.0	—	—	[27]
Sn (liquid)	—	—	—	—	1.7	—	—	[30]
Au (111)	—	—	—	—	3.7	—	—	[33]
Au (100)	—	—	—	—	3.0	—	—	[33]
Au (110)	—	—	—	—	2.0	—	—	[33]
Au	—	—	—	—	3.6	—	—	[33]
Al (111)	—	—	—	—	1.0	—	—	[33]

tering gas atoms which in turn bombard the target and release more secondary electrons in an avalanche process. Upon arrival at the substrate, such energy as they retain after collisions in the gas is liberated in the form of heat [38–43]. Many of the secondary electrons are thermalized by collisions in the gas, but even at high gas pressures, a substantial number of electrons retain full target potential upon impact at the substrates [41, 42].

2. Secondary Ions

Most of the data on ion emission from solids due to primary ion bombardment is to be found in the literature of secondary ion mass spectroscopy (SIMS). Most of this literature deals with the formation and emission of positive ions. However, in glow discharge sputtering, it is highly

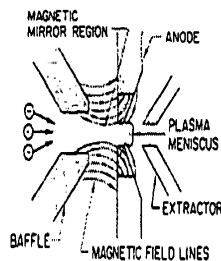


Fig. 6. Anode region of duoplasmatron showing constriction of plasma and plasma meniscus (from Brewer *et al.* [23]).

higher [15, 25] are obtained at about 20 keV beam energy through an aperture of 0.03-cm diameter with an energy spread of 10–50 eV [15]. The converging region of magnetic field lines acts as a magnetic mirror to reflect electrons back to the cathode region [23], enhancing ionization efficiency.

4. Other Ion Sources

Several additional ion source types will be mentioned, with references, to indicate the variety of approaches to generating ions. These are listed with the hope of stimulating novel applications to thin film deposition processes. The *glow discharge* ion source is simply a glow discharge between two plane electrodes with no magnetic field or thermionic cathode. One variation of this configuration is the *hollow anode* ion source in which the beam is extracted through a hole in the cathode plate [26, 27]. The *hollow cathode* ion source, of the same basic type, may be used in place of a thermionic cathode in applications where lifetime or contamination from the cathode are important [4, 28]. The *twin anode* or *electrostatic* ion source uses the geometrical arrangement of the anode surfaces within a surrounding cathode to produce long oscillatory electron trajectories, gaining enhanced ionization with no magnetic field [29].

The term *arc discharge* ion source applies to several configurations. In one type the desired material is vaporized from a crucible directly into a low voltage thermionically supported arc discharge. With some materials the arc is self sustaining with no support gas [30, 31]. No magnetic field is used. Ions are extracted with a low energy spread of 0.1–1.0 eV [31].

The *electrohydrodynamic* ion source [10] is a liquid-metal field emitting tip which generates a very high brightness, low current ion beam. A strong electric field pulls the liquid into a cusp-shaped tip less than 10^{-4} -cm diameter.

A vapor stream of atoms may be ionized by direct electron bombardment from a hot filament [32]. A variation of this technique, the *ionized cluster* source [33], vaporizes the desired material through a small orifice, inducing cluster formation as the vapor stream expands.

High multiply-charged ion states, for example Ar^{14+} , Kr^{17+} , Xe^{21+} ,

have been obtained by constraining the ions long enough for sequential ionization [34]. *Negative ion* beams may be generated by sputtering the desired material with a beam of low ionization potential material such as cesium [35], and may also be extracted from an off-axis aperture in a duoplasmatron [36]. *Very high current* hydrogen ion beams (several amperes) have been generated with a combined duoplasmatron and Penning ion source [37].

C. Beam Extraction and Control

1. Ion Extraction

Ions in the interior of the plasma diffuse to the plasma boundary, where they are extracted by an electric field. The rate of ion extraction is determined by Child's law of space charge limited current flow [4, 38]. In a planar geometry the space charge limited current density between two planes a distance d apart with potential difference V is

$$j = (4\epsilon_0/9)(2q/m)^{1/2}(V^{3/2}/d^2),$$

where ϵ_0 is the permeability of free space and q/m is the charge-to-mass ratio of the particles. This relationship determines the upper limit for planar current flow and demonstrates two important controls on the current density. Ion extraction from the plasma increases rapidly with increased extraction voltage and with decreased spacing between the plasma boundary and extraction electrode. For nonplanar geometries only the proportionality constant changes in Child's law, thus a given geometry may be characterized by the ratio $j/V^{3/2}$, the *perveance* [4].

Acceleration takes place mainly in the extraction region, since this is usually where the greatest potential drop occurs. However, the ion energy at the target is determined only by the potential difference between the target and the point of origin of the ion, which is usually within a few volts of anode potential. The usual arrangement is to have the target at ground potential and raise the entire source chamber to the desired beam voltage, with the extraction electrode at ground potential or lower.

As an example of extraction geometry, Fig. 7 shows the potential distribution through the extraction region of a Kaufman source [4]. The screen electrode is at the source potential (positive) and the accelerator or extraction electrode is negative. The screen voltage is lower than the anode voltage by the discharge voltage, with the difference between plasma potential and anode voltage not indicated. The extraction electrode is held negative, typically –200 V for source voltage of 1000 V, for two reasons. The rate of ion extraction is increased by a larger potential

The beam profile from a duoplasmatron or other single aperture source is usually close to Gaussian, determined more by the range of transverse velocities and the ion transport optics than by the initial profile at the extractor.

2. Beam Transport

Beam deflection is accomplished by transverse electric fields [42] and mass separation by magnetic fields [43]. If mass separation is desired with a straight trajectory, crossed electric and magnetic fields will select a particular velocity and deflect all others, acting as a mass separator [31, 44].

One type of focusing lens will be mentioned briefly. The Einzel, or uni-potential, lens consists of a decelerate section followed by an accelerate section back to the initial beam energy [24]. The field distribution defocuses the beam while it is at high energy and focuses while it is at low energy, resulting in a net focusing of the beam. Examples of using the Einzel lens to focus the beam from a single aperture source are given in Sections III.A and IV.A.

3. Neutralization

The above methods of deflecting and focusing an ion beam apply to a nonneutralized beam. With the broad beam from a Kaufman source, neutralization is necessary to avoid beam spreading by space charge repulsion. This is accomplished by adding electrons from a thermionic filament (Fig. 4) and monitoring the net current to the target or a beam probe. When the net current is zero, the arrival rate of ions equals that of electrons, but the ions are not neutralized by recombination since the mean free path for this process is much larger than the beam diameter [4]. The beam is itself a plasma, in which the electrons rapidly distribute to cancel net charge, thus electron injection does not have to be uniform. The neutralizer filament is sputtered by the beam, and contributes to contamination unless suitable masking is provided. An alternate method of injecting electrons into the beam is from a hollow cathode source (the plasma bridge neutralizer) which may be located outside the beam [4, 44a].

D. System Requirements

1. Materials

Materials in the ion source must be stable at the temperatures involved (several hundred degrees Celsius), have low sputtering yield if subjected to ion bombardment, and low susceptibility to corrosive gases, if used.

Particularly important components are the cathode filaments and electrode apertures. Thermionic cathodes are tantalum or tungsten wire [18], or barium oxide coated mesh [24]. Thermal cycling leads to embrittlement and failure, with exposure to oxygen or more reactive gases shortening filament life greatly. Magnetic fields may be supplied by an external solenoid, usually air cooled, or by permanent magnets, which do not have to be exposed to the plasma. Other surfaces may be molybdenum for thermal stability. In the Kaufman source the screen and accelerator grids span a large diameter, with a small separation, typically 0.1 cm. Thermal expansion leads to distortion, directly affecting extracted ion density and uniformity. These problems are minimized in ion thrusters by using dished molybdenum grids [4], such that thermal distortion occurs uniformly across the grids, but these are difficult to make accurately. Pyrolytic graphite provides the best combination of low thermal expansion, high thermal conductivity, and mechanical stiffness in flat grids [18]. For highest purity films it may be necessary to fabricate parts of the ion source out of materials that are compatible with the desired film [27, 45].

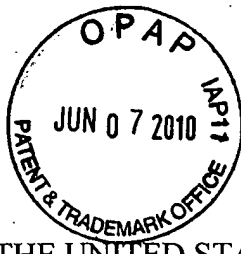
The lifetime of the source is limited by the hot cathode burning out or by buildup of sputtered material in the source, leading to shorting or to insulating coating of electrodes. Flaking of accumulated sputtered material may also cause shorts and insulating supports must be shielded from sputter coating. Lifetimes range from hours to months depending on operating conditions.

2. Vacuum and Gas

The gas pressure in the ion source is determined by the type of source and the ion density needed for the desired ion current. Therefore the pressure at the target is determined by the conductance of the ion source apertures and the pumping speed of the pump, assumed to be in the target region. Background gas in the path of the beam has two effects in addition to the effect of gas pressure on the source itself. Large angle collisions contribute slightly to beam divergence, and charge exchange collisions which result in fast neutrals and slow ions contribute to the sputtering rate at the target without registering as ion current to a probe [18]. The pressure must be below about 1 Pa to sustain a beam without excessive scattering, but is usually maintained around 0.1 Pa or lower to minimize divergence and contamination.

3. Electrical and Other Requirements

The electrical power requirements of the ion sources described above are straightforward. The filaments may be heated with ac or dc current of



21283/931A 3750 PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

ZHENGHE HAN et al.

Serial No.: 10/541,296

Filed: July 6, 2005

For: SURFACE MODIFICATION
METHOD IN FABRICATING HIGH
TEMPERATURE SUPER
CONDUCTIVE DEVICES

Art Unit: 1793

Examiner: Paul A. Wartalowicz

APPELLANT'S RESPONSE

Honorable Commissioner of Patents & Trademarks
P.O. Box 1450
Alexandria VA 22313-1450

Dear Sir:

In response to the Examiner's Answer dated April 5, 2010, submitted herewith are copies of selected portions of "Thin Film Processes", edited by John L. Vossen and Werner Kern and published by the Academic Press, Inc. in New York (R1) and "Ion Bombardment Modification of Surfaces: Fundamentals and Applications", edited by Orlando Auciello and Roger Kelly, published by Elsevier in Amsterdam in 1984 (R2). These two reference documents R1 and R2 will be utilized in Applicant's arguments which are set forth herein below.

Without going into the detail of each and every rejection presented by the Examiner, Appellant respectfully submits that essentially it is the Examiner's opinion, which is not supported by any documentation, that a particle beam generated by a plasma sputtering device is substantially the same as an ion beam, that the properties in the product produced by the utilization of an ion beam would be substantially or inherently the same as that of a plasma sputtering device and the product produced utilizing the plasma sputtering device has no advantages over one produces with an ion beam. Accordingly, it is the Examiner's opinion that Applicant's claims are all anticipated or obvious over the art cited by the Examiner.

In reply to this position by the Examiner, Appellant respectfully submits that a plasma sputtering beam and an ion beam are not equivalent. In particular, each have different properties and Appellant respectfully submits that plasma sputtering has advantages over ion beams. These two issues will be discussed at length below.

In particular, Appellant respectfully submits that for the ion beam generated from ion guns (also called ion sources), a low background gas pressure is usually maintained of about 0.1Pa or lower to minimize divergence of the beam and contamination (see R1, page 187, lines 35 and 36). Since the ion beam operates in a low background gas pressure, the energetic ions will travel a sufficient distance along a free path without collisions with the gas molecules. Therefore, the ion flux and the ion energy are independently controlled and the direction of ion impact on the surfaces is controlled (see R2, page 130, lines 19-23). Also, Appellant respectfully submits that a focus system of the ion source can decrease the divergence of the ion beam. For example, in a normal condition, the plasma edge beside the grid system in ion guns could form a proper shape, which gives the ion beam an initial convergence. Acceleration of the ions takes place mainly in the extraction region in the ion guns, since this is usually where the greatest potential drop occurs (see R1, page 183, lines 24-25). As a result, any ions leaving the discharged plasma and striking ground will have an energy corresponding to the anode potential. Still further, the ion beam has a direction which is well defined with narrow energy spread (see R2, page 132, lines 24-26).

In contrast to ion beams from an ion source, Appellant respectfully submits that for the particle beam generated from plasma sputtering systems, the background gas pressure is significantly higher than that of the ion beam. In particular, the gas pressure of the sputtering system usually ranges from a few millitorr to about 100 mTorr (see R1, page 12, lines 37-38). In some cases, Appellant respectfully submits that the gas pressure can even be the same as atmosphere for daily applications rather than the utilization in a vacuum chamber. Appellant respectfully further submits that in this range of gas pressure, the collisions between the ions and gas molecules will occur constantly. As a result of the collisions, the energy and direction of the ions will be different from the original values they were when accelerated by the electric field. Still further, there is no focus system in plasma sputtering systems and therefore they are simpler than ion beams and less costly. Also and as a result, the particle beam generated from plasma sputtering systems has a direction poorly defined with wide energy spread and is quite different from that of an ion beam generated from ion guns.

With the above in mind, Appellant respectfully submits that the direction of the ions in a single particle beam from plasma sputtering are random, while the direction of the ions in an ion beam from an ion gun are well defined. Also, the energy of the ions in a single particle beam from plasma sputtering is widely distributed while the energy of ions in an ion beam from ion guns is the same. Accordingly, Appellant respectfully submits that the properties of the two types of particle beams are quite different. As a result, Appellant respectfully submits that since the energy distribution of the plasma sputtering is widely distributed, the smoothness of the material surface can be more easily achieved. In contrast thereto, the focus tight high energy ion beam from ion guns has a tendency to cause an uneven surface because small areas of the surface are impacted with the high energy beam at a time.

In addition to the above, Appellant respectfully submits that the average number of atoms ejected from the target per incident ion is called the sputtering yield. Sputtering yield depends on the ion incident angle, which can be both calculated from theory (see R1, page 177, Fig. 5.2) and measured (see R2, page 2, Fig. 1.1). Still further, there is a maximum sputtering yield which can be achieved at a certain incident angle to the surface normal and the sputtering yield will be lower when the incident angle is some other value. Accordingly, when the target (processed material) surface is rough, the local normal directions of the different zones of the target surface are obviously different from each other. In this case, the sputtering yields of different zones of the target surfaces are not equal if the incident ions come from the same direction. However, if the directions of the ions are poorly defined, the sputtering yields of the different zones of the target surface can be uniform. Therefore, since plasma sputtering creates ions from different directions, it is easier to create a uniform surface with a particle beam generated by plasma sputtering.

In addition, Appellant respectfully submits there will be a shadow of sharp asperities where a well defined ion beam from an ion gun is not able to reach (see R2, page 233, Fig. 6.10). However, this problem can be handled when the ion directions of the particle beam from the plasma sputtering are poorly defined. Because the directions of the ions in the particle beam from plasma sputtering are random, the shadow from one incident direction can be reached by the ions in other directions. Therefore, the particle beam of plasma sputtering has the effect of smoothing the rough surface better than ion beams of ion guns.

Still further to the above, Appellant respectfully submits that the same things happen as described above in cases of changing the microstructure or internal defects of the target

because of the same reasons. In particular, the particle beam of plasma sputtering has better effect than the ion beam from ion guns. The more uniform arrival of ion density can be achieved with less shadow with the plasma sputtering since the ion directions of the particle beam from plasma sputtering are poorly defined.

From the above, Appellant respectfully submits that the advantages of ion beams coming from ion guns include small divergence angle, small energy distribution, individual and separate controlling energy and beam flow with the energies and the directions of the particles being concentrated. However, Appellant respectfully submits that these advantages of ion beams are not suitable for surface modification of a pre-formed material, especially not suitable for the modification of rough surfaces. As a result, Appellant respectfully submits that the disadvantages perceived by some of the particle beam from plasma sputtering being poorly defined and random, are in fact advantages since they are able to process a material surface to be smoother and more uniform than an ion beam.

By way of example, Appellant respectfully submits that an ion beam from an ion gun functions substantially the same as the bullets from a machine gun, whereas the particle beam from plasma sputtering functions similar to the bullets from a scatter gun. Clearly the bullets between these two types of guns are different in that the direction of the bullets from a scatter gun are rather random and therefore hit a large area, while the direction of the bullets from a machine gun are defined to form a line. As a result of the differences between a scatter gun and a machine gun, each is utilized for a particular purpose and cannot achieve the other's.

Based upon the discussion above, Appellant respectfully submits that the advantages remain in bombarding a high temperature superconductor, which cannot be produced with a particle beam produced by the apparatuses of the prior art. In particular, the advantages of a particle beam from plasma sputtering in fabricating and modifying a high temperature superconductor are as follows:

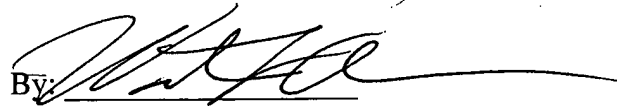
1. The structure of YBCO high temperature superconductors consist of many layers, including the substrate, buffer layers and YBCO superconductor layer. The substrate and buffer layers need to be cleaned, smooth and activated by the particle beams before the fabrication of an upper layer. Since the particle beam from sputtering is distributed in energy and arrives from random directions, smoothing and cleaning can be easily achieved. Still further, since the particle beam from plasma sputtering bombards a larger area, the modification speed is increased.

2. In the process of modifying the YBCO superconductor surface, the oxygen pressure should be high enough to prevent the degrading of the superconductivity. Appellant respectfully submits that a high gas pressure is not suitable for ion beams from ion guns as is discussed above and oxygen is usually harmful to the ion guns. In contrast thereto, a particle beam from plasma sputtering can function in such an atmosphere and can modify the surface of the superconductor device without degrading its superconductivity.

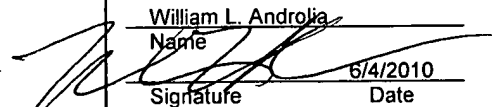
In view of the above, therefore, Appellant respectfully submits that ion beams are not substantially similar to particle beams from plasma sputtering and do not result in a substantially similar process. In addition, Appellant respectfully submits that in a method for surface modification in manufacturing high temperature superconducting devices, a particle beam from plasma sputtering has advantages over ion beams and provides a method utilizing a substantially simpler apparatus which can achieve the processing in less time. Therefore, Appellant respectfully submits that Appellant's invention as claimed by Appellant's claims 1 through 13 and 15 through 18 are not anticipated by nor obvious over the art cited by the Examiner.

Therefore, Appellant respectfully requests that the board favorably consider Appellant's remarks and find Appellant's invention as claimed patentably distinct from the art cited by the Examiner.

Respectfully submitted,

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BEAM MODIFICATION OF MATERIALS,1

ION BOMBARDMENT MODIFICATION OF SURFACES

Fundamentals and Applications

edited by



20149331N

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1

Chapter I

HISTORICAL OVERVIEW OF ION-INDUCED MORPHOLOGICAL MODIFICATION OF SURFACES

ORLANDO AUCIELLO

1.1 INTRODUCTION

This book is concerned with ion-bombardment modification of surfaces due mainly to erosional and depositional phenomena. Chemical, electrical, mechanical, etc. changes, due to ion bombardment of surfaces, are the subject of other reviews.

The two most important phenomena relating to ion bombardment modification of surfaces are sputtering and ion implantation. In spite of their similar degree of relevance, the evolution in the understanding of the underlying mechanisms has been quite different. Sputtering was observed by Grove, apparently for the first time, in 1853 (1) as the cause of metallic deposits on the glass walls of discharge tubes. However, it took almost half a century before sputtering was recognised (2) to be an effect caused by positive ions, from the discharge, hitting the cathode; and about a century before a quantitative description of this phenomenon started to be developed. By contrast, it can be said that the evolution in the understanding of the ion implantation process started with the theoretical works of Bohr (3) and Lindhard, Scharff, and Schiøtt (4), who set the bases for the understanding of the stopping power of high and low energy ions penetrating through matter. These works, supported by the first accurate experiments on ion ranges by Davies and coworkers (5, 6), initiated a comparatively faster development, with respect to sputtering, in ion implantation.

A historical overview of the main advances in the understanding of ion bombardment modification of surfaces, due to erosional and depositional phenomena is presented in this chapter. It will be followed by three chapters of a general nature, regarding the subject treated in this book (Chapters 2-4), four more on the fundamentals of surface modification (Chapters 5-8), and finally five on applications of modified surfaces (Chapters 9-13).

1.2 EROSION-INDUCED MORPHOLOGICAL CHANGES

Solid surfaces are generally eroded when bombarded with energetic particles, namely neutral atoms/molecules, ions, electrons, or photons. The phenomenon responsible for such erosion is sputtering, which, according to the present knowledge (see Chapter 2 of this book), presents several variants now known as collisional, thermal, electronic, and exfoliation sputtering. It can also be understood within the framework of two main concepts, physical and chemical sputtering. The former involves the transfer of kinetic energy from the incident particle to target atoms, which results in the ejection of atoms through the surface. The second is due to a chemical reaction between the impinging particles and target atoms, which leads to the formation of volatile molecules. Details about physical sputtering, from

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both the theoretical and experimental point of view, can be found in a recent comprehensive treatment of this subject (7). Chemical sputtering is also reviewed in ref. (7), Chapter 2 of this book, and in more recent work, related to fusion technology, by Auciello, Stangeby and Haasz (8, 9, 10), who have clarified previous experimental and conceptual inconsistencies, and discovered new aspects of the chemical sputtering phenomenon for carbonaceous materials.

It has been observed that both sputtering mechanisms mentioned above can produce morphological changes on surfaces. Changes induced by physical sputtering arise mainly due to the dependence of the sputtering yield (Y) on the angle of incidence (θ) of the primary beam with respect to the surface (Fig. 1.1). Such a dependence was first observed by Fetz (11), and confirmed later by other groups (12-14). It is important to notice that one reason for the lack of reproducibility in the data of Fig. 1.1 may be the influence of surface topography developed on bombarded surfaces during sputtering yield measurements, an effect to which no appropriate attention has been paid by the different groups.

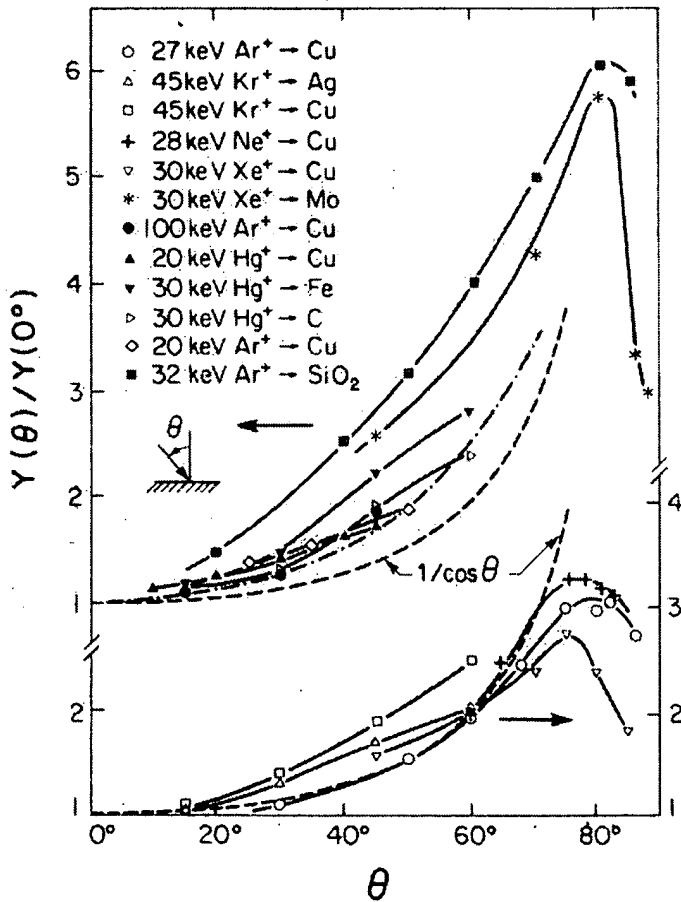


Fig. 1.1. Heavy-ion sputtering yields as a function of angle of incidence (7). The dash-and-dot curve represents theoretical calculations by Sigmund (7). The solid curves are drawn only to guide the eye.

4.2 DEPOSITION METHODS INVOLVING ION BOMBARDMENT

4.2.1. Radio-frequency bias sputtering

Many of the effects of ion bombardment during deposition were demonstrated using radio-frequency (rf) bias sputtering and later observed in other deposition systems. The equipment and principles of rf sputtering are thoroughly described elsewhere [1] and the technique will only be described here to bring out the capability for ion bombardment during film growth.

An rf diode sputtering system is shown schematically in Fig. 4.1. The target electrode (cathode) is driven by rf power to sustain a glow discharge plasma in the process gas. The cathode develops a negative dc voltage equal to about half the rf peak-to-peak voltage. Ions are accelerated across the cathode dark space to sputter atoms from the target surface. At a typical pressure of 4 Pa (30 mTorr), the sputtered atoms rapidly lose their ejection energy by collisions with the background gas [2], and diffuse to the substrates at essentially thermal energy. Ion bombardment of the substrates is provided by an rf bias voltage applied to the substrate electrode (anode), which develops a negative bias relative to the glow discharge. This potential difference accelerates ions from the plasma to the substrate, providing ion bombardment of the film during deposition. An applied substrate bias of -50 to -300 V is typically used with target voltages of -1000 to -3000V. Other energetic particles striking the growing film are: discharge ions reflected from the target as neutrals; secondary electrons accelerated from the target across the dark space; negative ions emitted from the target [3]; and charge exchange neutrals formed in the anode dark space [4]. Due to the charge exchange process in the anode dark space, very few discharge ions strike the substrate with the full bias voltage, but rather a broad, low energy distribution of ions and neutrals bombards the growing film [4]. Another complication is the lack of direct control over the plasma potential, which is positive with respect to the grounded chamber walls, and depends on the system geometry and gas pressure, typically 20 V at 4 Pa [5]. This plasma potential must be added to the applied substrate bias to determine the maximum ion energy striking the film.

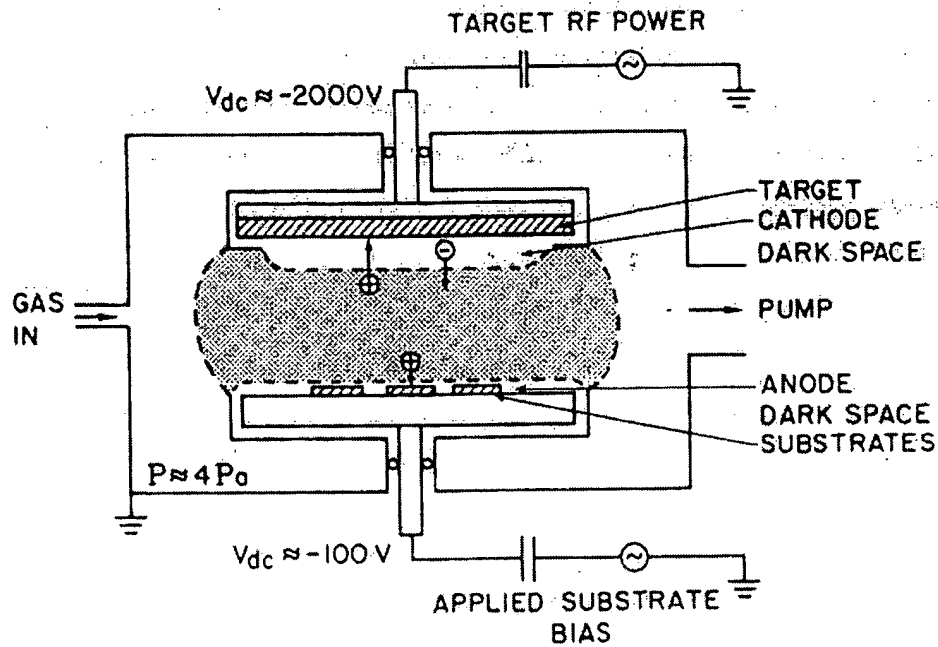


Fig. 4.1. Radio frequency (rf) diode sputtering system for thin film deposition. The dotted region is the discharge plasma.

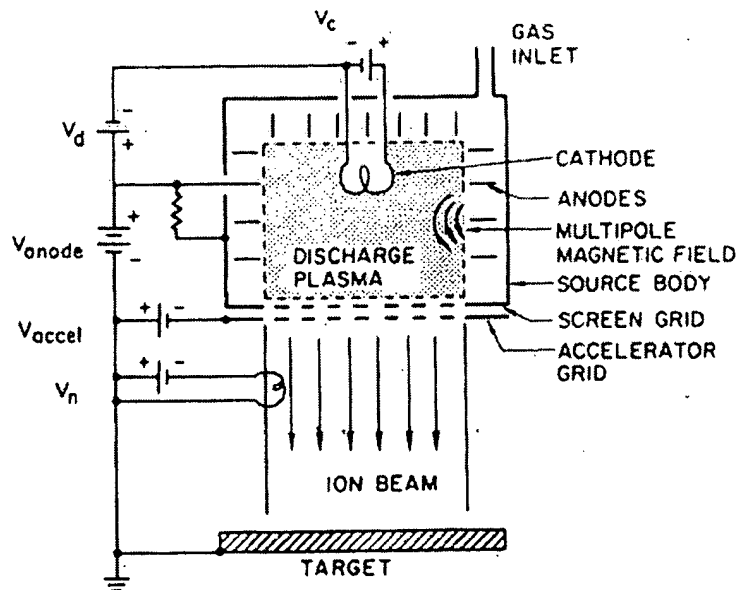


Fig. 4.2. Broad-beam multiaperture ion beam source [9].

Controlling the flux of ions bombarding the film in an rf diode system is not straightforward. Increasing the substrate bias voltage not only increases the bombarding ion energy, but also enhances the ion density in the glow discharge, thereby increasing the ion flux to the substrate. For this reason, the bombarding ion energy and flux are not independent parameters. Cuomo and Gambino [6] have successfully modeled the substrate ion flux as proportional to the one-half power of substrate bias voltage,

$$j \propto V_b^{1/2} \quad (1)$$

but to obtain quantitative flux values requires a detailed accounting of the geometry of the system. This difficulty, together with the broad energy distribution of particles striking the film, has limited the quantitative understanding of substrate bias effects, and the ability to translate data from one system to another.

4.2.2. Broad-beam ion sources

The broad-beam multiaperture electron bombardment ion source was invented in 1961 as an ion thruster for space propulsion [7]. An extensive effort followed to improve the efficiency of this ion source with the goal of obtaining the highest ion beam flux for a given gas flow and power input. These developments have yielded an ion source suitable for material processing, generating collimated, well-characterized ion beams from a wide choice of gas species [8]. The primary advantage of ion beam processing of materials lies in the control available with an ion beam as compared to other plasma processes. The ion flux and ion energy are easily measured and independently controlled, and the direction of ion impact on surfaces is controlled, since the beams operate in a low background gas pressure of typically 0.01 Pa ($\sim 10^{-4}$ Torr). The development of broad-beam ion sources and their applications to etching, surface compound layer formation, and thin film deposition are described in recent review articles [9]. The basic configuration of a broad-beam ion source is shown in Fig. 4.2, which illustrates a cylindrical unit generating a circular beam. The ion source is mounted in a vacuum chamber (not shown) capable of maintaining a background pressure of about 0.01 Pa ($\sim 10^{-4}$ Torr) at the operating conditions (generally a pumping speed of several hundred to several thousand

For many materials applications, a high ion flux is desired in order to carry out the etching/deposition process at a reasonable rate. For reference, 1 mA/cm^2 represents several monolayers equivalent of bombardment per second, and 10^{-4} Pa ($\sim 10^{-6} \text{ Torr}$) represents about one monolayer equivalent of background gas arrival rate per second. Therefore an ion flux of tenths of a mA/cm^2 or higher is necessary for surface treatment processes to occur at a rate exceeding the arrival rate of residual gases, for processing systems with base pressures of 10^{-5} Pa ($\sim 10^{-7} \text{ Torr}$). Also, many applications require low ion energy (several hundred eV or less) to minimize damage to substrates. This combination of high ion flux at low energy is difficult to achieve with the conventional dual grid ion source of Fig. 4.2 because the ion flux is space charge limited by the grid separation. The maximum ion flux is determined by Child's Law [9,10]:

$$j_{\text{max}} = (4\epsilon_0/9)(2e/m)^{1/2} V^{3/2}/l^2, \quad (2)$$

where j_{max} is the maximum ion flux flowing between two planes, V is the potential difference between the planes, l is the spacing between the planes, e/m is the charge-to-mass ratio of the ions, and ϵ_0 is the permittivity of space. For practical ion source configurations, l is approximately given by the spacing between the screen and accelerator grids [9]. This space charge limit sets a ceiling on the ion flux obtainable at a given ion energy, and becomes a severe limit at low energy. For example, with a dual grid system which produces 1.5 mA/cm^2 at 1000 eV ion energy, the ion flux available at 100 eV follows from Eq. 2 as only 0.05 mA/cm^2 . Several improvements in the low energy performance have been made and recently described [9,11].

The output of a broad-beam ion source is an ion beam of well-defined direction and low energy spread. Beam divergence angles can be as low as several degrees, and energy spreads are typically 10 eV [9]. In addition to the ion flux, a substantial neutral gas flow passes through the extraction grid system, since the grids have a high fraction of open area (50-60%). For many materials applications, however, this background gas flux does not greatly affect the process, as the gas is usually an inert or molecular species of low chemical reactivity. The background pressure is

very low (0.01 Pa , $\sim 10^{-4} \text{ Torr}$) compared to a typical rf sputtering or etching plasma ($1\text{--}10 \text{ Pa}$, $\sim 10\text{--}100 \text{ mTorr}$).

This low pressure, combined with the short ion acceleration distance between the grids (about 1 mm), is responsible for the low energy spread. Other species present in the beam include: low energy electrons with a Maxwellian temperature of several eV [8]; charge exchange neutrals caused by collisions of positive beam ions with background gas atoms [12]; and sputtered atoms from the target surface bombarded by the ion beam. Therefore, the ion beam processing environment is characterized by an ion flux of well-defined intensity, energy and direction, with relatively low power input to the substrate from other energetic species. This situation creates a suitable environment for quantitative materials processing by controlled ion bombardment.

The two main configurations for using broad beam ion sources for ion bombardment during film deposition are shown in Figs. 4.3 and 4.4. In the dual ion beam system (Fig. 4.3), an inert or reactive ion beam sputters a target material to produce a deposition flux of atoms onto the substrate. Simultaneously, a second ion source aimed at the substrate supplies an ion beam of inert or reactive ions to bombard the growing film. In the example shown, the substrate holder is equipped with a crystal rate monitor and an ion current monitor to measure the incident atom and ion fluxes directly. These features provide a proper characterization of the incident particle flux onto the film surface. In the second configuration (Fig. 4.4), an ion source is used in conjunction with a vapor source, such as an electron beam evaporator, to add ion bombardment capability to another widely used deposition technique. This configuration is sometimes referred to as "ion assisted deposition". Here also the energy, flux and direction of the bombarding ions are fully characterized and independent of the vapor source. This configuration has also been applied in the technique of molecular beam epitaxy (MBE) with simultaneous ion beam doping, although broad-beam ion sources are not generally used in MBE. In both of these configurations, the arrival flux of atoms and the ion bombardment have different angles of incidence on the substrate. This can cause anisotropic properties in the film plane and may require rotation of the substrate if isotropy in the plane is required.

the x axis is given by $\cos \alpha = p_1 c(y)$ and thus $p_1 = \frac{\cos \alpha}{c(y)} = \text{constant}$.

If in two neighbouring horizontal strata the wave speeds are $c(y_1)$ and $c(y_2)$, then from the constancy of p_1 it is readily observed that, at the interface

$$\frac{\cos \alpha_1}{\cos \alpha_2} = \frac{c(y_1)}{c(y_2)} \quad (34)$$

which is Snell's law in optics.

To conclude this part of the discussion it is to be noted that a reasonably detailed account of general wave front propagation and the role of characteristic equations in following this propagation has been given. In the next section it will be shown how sputter erosion (and other surface modifying processes) is a specific example of such propagation and, consequently, how the morphological development of sputter eroded surface can be predicted from the general techniques just examined. Moreover it will be shown that the several situations discussed above each have their analogues in the sputter erosion area and that the historical developments outlined in the first section can be fully described by general wave propagation formalisms. Given this underlying unified approach some problems, not previously addressed in sputter erosion theory, can be tackled and these potential applications are outlined later in the chapter.

5.4 SPUTTER EROSION AND OTHER SURFACE MODIFICATION PROCESSES

The fundamental processes of sputtering have been fully considered in Section 5.1 and here we will merely use some of the major results of that discussion.

Thus, we note that for an elemental crystalline target of surface orientation (hkl) irradiated at temperature T with atoms of energy E and mass M , incident at a polar angle θ to the surface normal and at azimuthal angle ϕ (defined with respect to a selected crystalline direction) the total sputtering yield Y in atoms ejected per ion must be written as $Y((h,k,l), T, E, M, \theta, \phi)$ for that target material. Further complexity results if one is interested in the double differential yield $\frac{d^2 Y}{dE d\Omega}$ for atoms ejected with energies in the range (E, dE) and over a specified solid angle $d\Omega$.

For initial simplification however we may consider the case of a random (amorphous) target irradiated at fixed temperature with monoenergetic ions of a single species. In this case, all but the dependence upon the polar angle θ vanishes and $Y = Y(\theta)$. A typical form for $Y(\theta)$ is shown schematically in figure 5.2, which reveals that in general $Y(\theta)$ increases from a minimum for $\theta = 0$ (normal incidence) to a maximum, via a relation somewhat like $Y(\theta) = Y(0) \sec^{-n} \theta$, to a maximum at $\theta = \pm \theta_p$ and then declines rather rapidly towards zero as $\theta \rightarrow \pm \pi/2$ (grazing incidence).

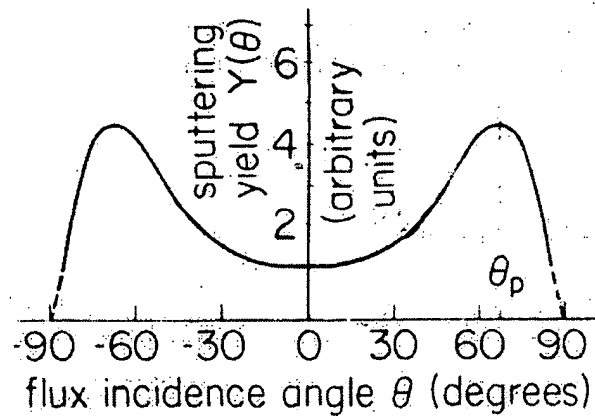


Fig. 5.2 Typical dependence of sputtering yield $Y(\theta)$ with flux incidence angle to surface normal.

If again, for simplification, we consider the case of irradiation by a uniform ion flux density J (ions. $\text{cm}^{-2}\text{sec}^{-1}$) incident in the $-Oz$ direction on to a surface plane inclined at angle θ to the xOy plane, then the ion flux falling upon unit area of this plane is $J\cos\theta$. The rate of atomic sputtering is thus $J.Y(\theta)\cos\theta$ since the ion flux J makes an angle θ to the surface normal. The linear rate of surface erosion, for a substrate of atomic density N is thus

$$\rho_n = \frac{JY(\theta)\cos\theta}{N} \quad (35)$$

By definition, since atoms are ejected in an averaged model of sputtering, from the surface atomic plane, the erosion process occurs normal to the surface. thus, equation (35) displays the speed of recession of a surface point along the normal direction.

In general the ion flux J may be spatially non-uniform, distributed in direction and variable in time. Thus the differential erosion rate must be written

$$d\rho_n = \frac{J(x,y,z,t)d\omega Y(\theta)\cos\theta}{N} \quad (36a)$$

where $J(x,y,z,t)$ is the partial instantaneous ion flux incident in a solid angle $d\omega$ about the incidence direction θ .

The total erosion rate ρ_n thus

$$\rho_n = \int_{-\pi/2}^{+\pi/2} \frac{J(x,y,z,t) Y(\theta)\cos\theta}{N} d\omega \quad (36b)$$

where the limits to the integral indicate that only ions incident to a surface point from the hemisphere above the surface point may be counted.

Equation (36b) not only accounts for a general surface where all surface points are accessible to the distributed ion flux but also for surface contours where elevated regions

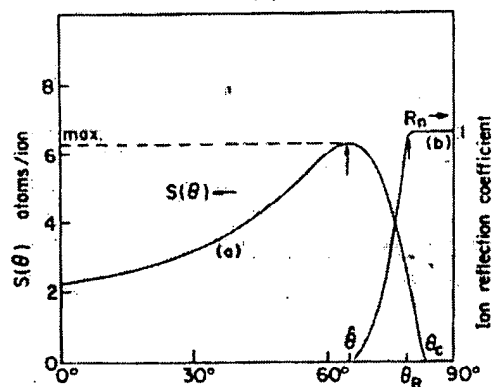


Fig. 6.9 General shape of the functional dependence of (a) the sputtering yield S with respect to angle of incidence of the ion beam with respect to the surface normal); and (b) ion reflection coefficient R_n vs. θ . Three characteristic angles are indicated (see text) (O. Auciello (26)).

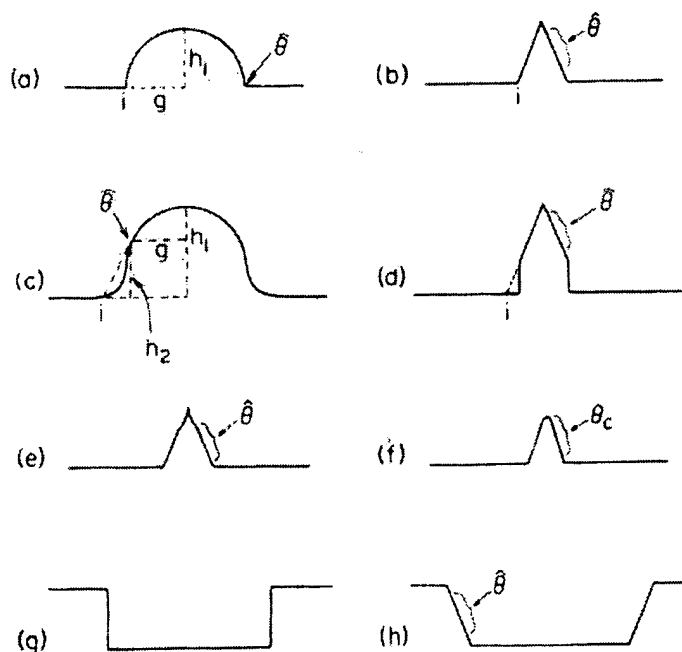


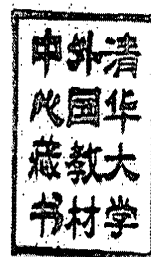
Fig. 6.10 Sketches relevant to the bombardment-induced evolution of asperities and depressions. (a) An asperity of width g and height h_1 which is everywhere convex-up and has a basal slope θ . (b) The pyramid into which (a) would evolve if intersection i moved sufficiently far. (c) A more generalized feature which is convex-up at its center and passes through a slope θ at some intermediate width g and height h_2 . (d) A possible intermediate stage of the bombardment-induced evolution of (c). (e) A pyramid which has a rounded tip, again due to an appropriate fluctuation. (f) A pyramid which has vertical slopes such as is encountered during the fabrication of microcircuitry. (g) A depression with vertical slopes such as is encountered during the fabrication of microcircuitry. (h) The steady-state form of a depression which results owing to appropriate fluctuations in the sputtering process. (Kelly and Auciello (17)).

THIN FILM PROCESSES

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Contents

<i>List of Contributors</i>	ix
<i>Preface</i>	xi

Part I

I-1 Introduction

J. L. Vossen

References	5
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Part II PHYSICAL METHODS OF FILM DEPOSITION

II-1 Glow Discharge Sputter Deposition

J. L. Vossen and J. J. Cuomo

I. Introduction	12
II. Physical and Chemical Effects of Ion Bombardment on Surfaces	14
III. Glow Discharges	24
IV. Equipment Configuration	31
V. Preconditioning of Targets, Substrates, and Systems for Film Deposition.	41
VI. The Sputtering Gas	46
VII. Deposition with Simultaneous Ion Bombardment of the Substrate and Growing Film	50
VIII. Rate and Uniformity of Deposition	61
IX. Conclusion	62
References	62

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Glow Discharge Sputter Deposition

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I. Introduction	12
II. Physical and Chemical Effects of Ion Bombardment on Surfaces	14
A. Emission of Neutral Particles—The Sputtering Yield	14
B. Emission of Other Particles	16
C. Emission of Radiation	20
D. Ion Implantation	20
E. Altered Surface Layers and Diffusion	21
F. Dissociation Processes	22
G. Chemical Sputtering	23
III. Glow Discharges	24
A. DC Glow Discharges	24
B. Low-Frequency AC Glow Discharges	27
C. RF Glow Discharges	27
D. Discharge Supporting Modes	29
IV. Equipment Configuration	31
A. Target Assemblies	31
B. Power Supplies	33
C. Instrumentation and Control	36
D. Substrate Heaters	37
E. Wall Losses	39
F. Shields and Shutters	39
G. Deposition Sources for Bias Sputtering and Ion Plating	39
H. Scale-Up Problems	40
V. Preconditioning of Targets, Substrates, and Systems for Film Deposition	41
A. Target Materials	41

B. Presputtering of Targets	42
C. Sputter Etching of Substrates	42
VI. The Sputtering Gas	46
A. Effects of Gas Species, Pressure, and Flow	46
B. Sources of Gas Contamination	46
C. Getter Sputtering	47
D. Reactive Sputtering	48
VII. Deposition with Simultaneous Ion Bombardment of the Substrate and Growing Film	50
A. Plasma, Floating, and Bias Potentials	50
B. Gas Incorporation and Desorption	58
C. Stoichiometry of Films	60
D. Physical Film Properties	60
VIII. Rate and Uniformity of Deposition	61
IX. Conclusion	62
References	62

I. INTRODUCTION

Over the past 20 years or so there have been numerous reviews of sputtering and sputtering processes for film deposition [1-15]. In this chapter we shall take a somewhat different viewpoint than those of most earlier reviewers. We shall attempt to treat this very complex subject from a process viewpoint. That is, we shall discuss the interactions of the process parameters to expose the many permutations and combinations that are available to control the properties of thin films.

Because there are so many interactions among parameters in sputtering systems, it is impossible to separate them completely. Thus, there are necessary, but regrettable references made to later sections throughout the chapter. In an attempt to minimize any confusion that this may cause, we shall give a brief, simple overview of the subject in this section before going to the more detailed discussions.

Figure 1 represents a greatly simplified cross section of a sputtering system. Typically, the target (a plate of the material to be deposited or the material from which a film is to be synthesized) is connected to a negative voltage supply (dc or rf). The substrate holder faces the target. The holder may be grounded, floating, biased, heated, cooled, or some combination of these. A gas is introduced to provide a medium in which a glow discharge can be initiated and maintained. Gas pressures ranging from a few millitorr to about 100 mTorr are used. The most common sputtering gas is argon.

When the glow discharge is started, positive ions strike the target plate and remove mainly neutral target atoms by momentum transfer, and these

II-1. GLOW DISCHARGE SPUTTER DEPOSITION

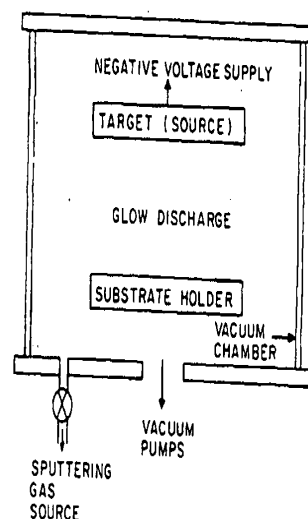


Fig. 1. Simplified cross section of a sputtering system.

condense into thin films. There are, in addition, other particles and radiation produced at the target, all of which may affect film properties (secondary electrons and ions, desorbed gases, x rays, and photons). The electrons and negative ions are accelerated toward the substrate platform and bombard it and the growing film. In some instances, a bias potential (usually negative) is applied to the substrate holder, so that the growing film is subject to positive ion bombardment. This is known variously as *bias sputtering* or *ion plating*. Initially, the term "ion plating" referred to a process in which the deposition source was a thermal evaporation filament instead of a sputtering target and the substrates were connected to a dc sputtering target [16], but it has sometimes been applied to any process in which the substrate is subjected to purposeful ion bombardment during film growth in a glow discharge environment [17].

In some cases, gases or gas mixtures other than Ar are used. Usually this involves some sort of *reactive sputtering* process in which a compound is synthesized by sputtering a metal target (e.g., Ti) in a reactive gas (e.g., O_2 or Ar- O_2 mixtures) to form a compound of the metal and the reactive gas species (e.g., TiO_2). Reactive sputtering is also used to replenish constituents of compound targets lost by dissociation. The reactive version of ion plating is sometimes known as *activated reactive evaporation* [18], but this terminology is more often applied to processes in which an evaporant passes through a glow discharge in transit to an electrically floating or grounded substrate. Reactive sputtering should not be confused with *chemical sputtering* in which the reactive gas (e.g., O_2) reacts with the target surface (e.g., C) to form volatile compounds (e.g.,

CO) that are pumped away [1]. Chemical sputtering is more properly related to ion etching processes (see Chapter V-2).

We shall consider in detail the complex interplay among target kinetics, glow discharge phenomena, substrate conditions, equipment configuration, etc. that bear on the ability to control the properties of thin films.

II. PHYSICAL AND CHEMICAL EFFECTS OF ION BOMBARDMENT ON SURFACES

In sputter deposition, surfaces subject to ion bombardment are usually considered as the source of material from which films are grown. In addition to the neutral (sputtered) material liberated from the bombarded surface which eventually condenses as a film, there are numerous other events that can occur at the target surface which may influence the growth of films profoundly. These include: secondary electron emission, secondary positive and/or negative ion emission, emission of radiation (photons, x rays), reflection of incident particles, heating, chemical dissociation or reaction, bulk diffusion, crystallographic changes, and reflection of some of the emitted particles back to the bombarded surface (backscattering). It should be noted that all of these same phenomena apply to sputter-etching processes (Chapter V-2) in which the workpiece is a sputtering target and to substrates in most glow discharge deposition processes. (As will be shown later, any material body immersed in a glow discharge acquires a negative potential with respect to its surroundings and must be considered a sputtering target.)

There have been several recent comprehensive reviews of the kinetics involved when a surface is ion bombarded [3, 6, 8, 12]. Therefore, we shall review them only briefly, emphasizing those target effects that can affect the way in which films grow.

A. Emission of Neutral Particles—The Sputtering Yield

The sputtering yield is defined as the number of atoms ejected from a target surface per incident ion. It is the most fundamental parameter of sputtering processes. Yet all of the surface interaction phenomena involved that contribute to the yield of a given surface are not completely understood. Despite this, an impressive body of literature exists showing the yield to be related to momentum transfer from energetic particles to target surface atoms. There is a threshold for sputtering that is approximately equal to the heat of sublimation. In the energy range of practical interest for sputtering processes (10–5000 eV), the yield increases with

incident ion energy, and with the mass and d-shell filling of the incident ion [19, 20].

The sputtering yield determines the erosion rate of sputtering targets; and largely, but not completely, determines the deposition rate of sputtered films. Several compilations of experimental sputtering yield and related data have been published [3, 5, 6, 21, 22]. All sputtering yields and related data should be used with caution. In glow discharge systems, bombarding ions are by no means monoenergetic, and it is not necessarily valid to use yield values for pure metals when alloys, compounds, or mixtures are sputtered. As will be shown, the sputtering yield of material A from a matrix of A + B is often very different from the sputtering yield of A from a matrix of A. Also, when sputtering yields of compounds are given, dissociation reactions are often ignored. Despite this, tabulations of sputtering yields are useful, if only to give a rough indication of the deposition or etch rate that might be expected for a given material. Tables I–III give a compilation of sputtering yields and relative film deposition

Table I
Sputtering Yield of Elements at 500 eV

Gas	He	Ne	Ar	Kr	Xe	Reference
Element						
Be	0.24	0.42	0.51	0.48	0.35	[23]
C	0.07	—	0.12	0.13	0.17	[23]
Al	0.16	0.73	1.05	0.96	0.82	[23]
Si	0.13	0.48	0.50	0.50	0.42	[23]
Ti	0.07	0.43	0.51	0.48	0.43	[23]
V	0.06	0.48	0.65	0.62	0.63	[23]
Cr	0.17	0.99	1.18	1.39	1.55	[23]
Mn	—	—	—	1.39	1.43	[23]
Mn	—	—	1.90	—	—	[24]
Bi	—	—	6.64	—	—	[24]
Fe	0.15	0.88	1.10	1.07	1.00	[23]
Fe	—	0.63	0.84	0.77	0.88	[25]
Co	0.13	0.90	1.22	1.08	1.08	[23]
Ni	0.16	1.10	1.45	1.30	1.22	[23]
Ni	—	0.99	1.33	1.06	1.22	[25]
Cu	0.24	1.80	2.35	2.35	2.05	[23]
Cu	—	1.35	2.0	1.91	1.91	[25]
Cu (111)	—	2.1	—	2.50	3.9	[26]
Cu	—	—	1.2	—	—	[27]
Ge	0.08	0.68	1.1	1.12	1.04	[23]
Y	0.05	0.46	0.68	0.66	0.48	[23]
Zr	0.02	0.38	0.65	0.51	0.58	[23]

Table I (Continued)

Gas	He	Ne	Ar	Kr	Xe	Reference
Nb	0.03	0.33	0.60	0.55	0.53	[23]
Mo	0.03	0.48	0.80	0.87	0.87	[23]
Mo	—	0.24	0.64	0.59	0.72	[25]
Ru	—	0.57	1.15	1.27	1.20	[23]
Rh	0.06	0.70	1.30	1.43	1.38	[23]
Pd	0.13	1.15	2.08	2.22	2.23	[23]
Ag	0.20	1.77	3.12	3.27	3.32	[23]
Ag	1.0	1.70	2.4	3.1	—	[27]
Ag	—	—	—	—	—	[28]
Sm	0.05	0.69	0.80	1.09	1.28	[23]
Gd	0.03	0.48	0.83	1.12	1.20	[23]
Dy	0.03	0.55	0.88	1.15	1.29	[23]
Er	0.03	0.52	0.77	1.07	1.07	[23]
Hf	0.01	0.32	0.70	0.80	—	[23]
Ta	0.01	0.28	0.57	0.87	0.88	[23]
W	0.01	0.28	0.57	0.91	1.01	[23]
Re	0.01	0.37	0.87	1.25	—	[23]
Os	0.01	0.37	0.87	1.27	1.33	[23]
Ir	0.01	0.43	1.01	1.56	1.56	[23]
Pt	0.03	0.63	1.40	1.82	1.93	[23]
Au	0.07	1.08	2.40	3.06	3.01	[23]
Au	0.10	1.3	2.5	—	7.7	[29]
Pb	1.1	—	2.7	—	—	[27]
Th	0.0	0.28	0.62	0.96	1.05	[23]
U	—	0.45	0.85	1.30	0.81	[23]
Sb	—	—	2.83	—	—	[24]
Sn (solid)	—	—	1.2	—	—	[30]
Sn (liquid)	—	—	1.4	—	—	[30]

rates. The latter have been normalized to the sputtering yields of pure metals [21]. All target materials are polycrystalline unless otherwise indicated. Since sputtering targets are held at high negative potentials, secondary electrons are accelerated away from the target surface with an initial energy equal to the target potential. As will be shown in Section III. A, these electrons help to sustain the glow discharge by ionization of neutral sput-

1. Secondary Electrons

B. Emission of Other Particles

2. Secondary Ions

Most of the data on ion emission from solids due to primary ion bombardment is to be found in the literature of secondary ion mass spectroscopy (SIMS). Most of this literature deals with the formation and emission of positive ions. However, in glow discharge sputtering, it is highly

of electrons retain full target potential upon impact at the substrates [41, 42]. collisions in the gas, but even at high gas pressures, a substantial number form of heat [38-43]. Many of the secondary electrons are thermalized by such energy as they retain after collisions in the gas is liberated in the secondary electrons in an avalanche process. Upon arrival at the substrate, turning gas atoms which in turn bombard the target and release more secondary electrons.

Gas	He	N	Ne	N ₂	Ar	Kr	Xe	Reference
Fe	—	—	0.85	—	1.33	1.42	1.82	[25]
Fe	—	0.55	—	0.78	—	—	—	[3]
Ni	—	—	1.22	—	2.21	1.76	2.26	[25]
Ni	—	0.74	—	1.05	—	—	—	[3]
Ni	—	—	—	—	2.0	2.0	2.0	[26]
Cu	—	—	1.88	—	2.85	3.42	3.6	[25]
Cu	—	1.5	—	—	—	—	—	[3]
Cu	—	—	—	—	3.2	2.5	—	[27]
Cu (111)	—	—	2.75	—	4.5	4.65	6.05	[26]
Cu	—	—	—	1.95	—	—	—	[31]
Mo	—	—	0.49	—	1.13	1.27	1.60	[25]
Mo	—	0.16	—	0.3	—	—	—	[3]
Ag	1.8	—	2.4	—	3.8	4.7	—	[27]
Sn	—	—	—	—	0.8	—	—	[32]
W	—	0.18	—	0.2	—	—	—	[3]
Au	—	—	—	—	1.0	—	—	[32]
Au	0.3	—	—	—	4.9	—	—	[29]
Pb	1.5	—	—	—	3.0	—	—	[27]
Sn (liquid)	—	—	—	—	1.7	—	—	[30]
Au (111)	—	—	—	—	3.7	—	—	[33]
Au (100)	—	—	—	—	3.0	—	—	[33]
Au (110)	—	—	—	—	2.0	—	—	[33]
Au	—	—	—	—	3.6	—	—	[33]
Al (111)	—	—	—	—	1.0	—	—	[33]

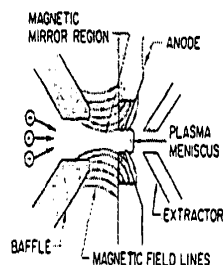


Fig. 6. Anode region of duoplasmatron showing constriction of plasma and plasma meniscus (from Brewer *et al.* [23]).

higher [15, 25] are obtained at about 20 keV beam energy through an aperture of 0.03-cm diameter with an energy spread of 10–50 eV [15]. The converging region of magnetic field lines acts as a magnetic mirror to reflect electrons back to the cathode region [23], enhancing ionization efficiency.

4. Other Ion Sources

Several additional ion source types will be mentioned, with references, to indicate the variety of approaches to generating ions. These are listed with the hope of stimulating novel applications to thin film deposition processes. The *glow discharge* ion source is simply a glow discharge between two plane electrodes with no magnetic field or thermionic cathode. One variation of this configuration is the *hollow anode* ion source in which the beam is extracted through a hole in the cathode plate [26, 27]. The *hollow cathode* ion source, of the same basic type, may be used in place of a thermionic cathode in applications where lifetime or contamination from the cathode are important [4, 28]. The *twin anode* or *electrostatic* ion source uses the geometrical arrangement of the anode surfaces within a surrounding cathode to produce long oscillatory electron trajectories, gaining enhanced ionization with no magnetic field [29].

The term *arc discharge* ion source applies to several configurations. In one type the desired material is vaporized from a crucible directly into a low voltage thermionically supported arc discharge. With some materials the arc is self sustaining with no support gas [30, 31]. No magnetic field is used. Ions are extracted with a low energy spread of 0.1–1.0 eV [31].

The *electrohydrodynamic* ion source [10] is a liquid-metal field emitting tip which generates a very high brightness, low current ion beam. A strong electric field pulls the liquid into a cusp-shaped tip less than 10^{-4} -cm diameter.

A vapor stream of atoms may be ionized by direct electron bombardment from a hot filament [32]. A variation of this technique, the *ionized cluster* source [33], vaporizes the desired material through a small orifice, inducing cluster formation as the vapor stream expands.

High multiply-charged ion states, for example Ar^{14+} , Kr^{17+} , Xe^{21+} ,

have been obtained by constraining the ions long enough for sequential ionization [34]. *Negative ion* beams may be generated by sputtering the desired material with a beam of low ionization potential material such as cesium [35], and may also be extracted from an off-axis aperture in a duoplasmatron [36]. *Very high current* hydrogen ion beams (several amperes) have been generated with a combined duoplasmatron and Penning ion source [37].

C. Beam Extraction and Control

1. Ion Extraction

Ions in the interior of the plasma diffuse to the plasma boundary, where they are extracted by an electric field. The rate of ion extraction is determined by Child's law of space charge limited current flow [4, 38]. In a planar geometry the space charge limited current density between two planes a distance d apart with potential difference V is

$$j = (4\epsilon_0/9)(2q/m)^{1/2}(V^{3/2}/d^2),$$

where ϵ_0 is the permeability of free space and q/m is the charge-to-mass ratio of the particles. This relationship determines the upper limit for planar current flow and demonstrates two important controls on the current density. Ion extraction from the plasma increases rapidly with increased extraction voltage and with decreased spacing between the plasma boundary and extraction electrode. For nonplanar geometries only the proportionality constant changes in Child's law, thus a given geometry may be characterized by the ratio $j/V^{3/2}$, the *perveance* [4].

Acceleration takes place mainly in the extraction region, since this is usually where the greatest potential drop occurs. However, the ion energy at the target is determined only by the potential difference between the target and the point of origin of the ion, which is usually within a few volts of anode potential. The usual arrangement is to have the target at ground potential and raise the entire source chamber to the desired beam voltage, with the extraction electrode at ground potential or lower.

As an example of extraction geometry, Fig. 7 shows the potential distribution through the extraction region of a Kaufman source [4]. The screen electrode is at the source potential (positive) and the accelerator or extraction electrode is negative. The screen voltage is lower than the anode voltage by the discharge voltage, with the difference between plasma potential and anode voltage not indicated. The extraction electrode is held negative, typically –200 V for source voltage of 1000 V, for two reasons. The rate of ion extraction is increased by a larger potential

The beam profile from a duoplasmatron or other single aperture source is usually close to Gaussian, determined more by the range of transverse velocities and the ion transport optics than by the initial profile at the extractor.

2. Beam Transport

Beam deflection is accomplished by transverse electric fields [42] and mass separation by magnetic fields [43]. If mass separation is desired with a straight trajectory, crossed electric and magnetic fields will select a particular velocity and deflect all others, acting as a mass separator [31, 44].

One type of focusing lens will be mentioned briefly. The Einzel, or unipotential, lens consists of a decelerate section followed by an accelerate section back to the initial beam energy [24]. The field distribution defocuses the beam while it is at high energy and focuses while it is at low energy, resulting in a net focusing of the beam. Examples of using the Einzel lens to focus the beam from a single aperture source are given in Sections III.A and IV.A.

3. Neutralization

The above methods of deflecting and focusing an ion beam apply to a nonneutralized beam. With the broad beam from a Kaufman source, neutralization is necessary to avoid beam spreading by space charge repulsion. This is accomplished by adding electrons from a thermionic filament (Fig. 4) and monitoring the net current to the target or a beam probe. When the net current is zero, the arrival rate of ions equals that of electrons, but the ions are not neutralized by recombination since the mean free path for this process is much larger than the beam diameter [4]. The beam is itself a plasma, in which the electrons rapidly distribute to cancel net charge, thus electron injection does not have to be uniform. The neutralizer filament is sputtered by the beam, and contributes to contamination unless suitable masking is provided. An alternate method of injecting electrons into the beam is from a hollow cathode source (the plasma bridge neutralizer) which may be located outside the beam [4, 44a].

D. System Requirements

1. Materials

Materials in the ion source must be stable at the temperatures involved (several hundred degrees Celsius), have low sputtering yield if subjected to ion bombardment, and low susceptibility to corrosive gases, if used.

Particularly important components are the cathode filaments and electrode apertures. Thermionic cathodes are tantalum or tungsten wire [18], or barium oxide coated mesh [24]. Thermal cycling leads to embrittlement and failure, with exposure to oxygen or more reactive gases shortening filament life greatly. Magnetic fields may be supplied by an external solenoid, usually air cooled, or by permanent magnets, which do not have to be exposed to the plasma. Other surfaces may be molybdenum for thermal stability. In the Kaufman source the screen and accelerator grids span a large diameter, with a small separation, typically 0.1 cm. Thermal expansion leads to distortion, directly affecting extracted ion density and uniformity. These problems are minimized in ion thrusters by using dished molybdenum grids [4], such that thermal distortion occurs uniformly across the grids, but these are difficult to make accurately. Pyrolytic graphite provides the best combination of low thermal expansion, high thermal conductivity, and mechanical stiffness in flat grids [18]. For highest purity films it may be necessary to fabricate parts of the ion source out of materials that are compatible with the desired film [27, 45].

The lifetime of the source is limited by the hot cathode burning out or by buildup of sputtered material in the source, leading to shorting or to insulating coating of electrodes. Flaking of accumulated sputtered material may also cause shorts and insulating supports must be shielded from sputter coating. Lifetimes range from hours to months depending on operating conditions.

2. Vacuum and Gas

The gas pressure in the ion source is determined by the type of source and the ion density needed for the desired ion current. Therefore the pressure at the target is determined by the conductance of the ion source apertures and the pumping speed of the pump, assumed to be in the target region. Background gas in the path of the beam has two effects in addition to the effect of gas pressure on the source itself. Large angle collisions contribute slightly to beam divergence, and charge exchange collisions which result in fast neutrals and slow ions contribute to the sputtering rate at the target without registering as ion current to a probe [18]. The pressure must be below about 1 Pa to sustain a beam without excessive scattering, but is usually maintained around 0.1 Pa or lower to minimize divergence and contamination.

3. Electrical and Other Requirements

The electrical power requirements of the ion sources described above are straightforward. The filaments may be heated with ac or dc current of

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